PB-251 131

DETERMINATION OF INCINERATOR OPERATING CONDITIONS NECESSARY FOR SAFE DISPOSAL OF PESTICIDES

Thomas L. Ferguson, et al

Midwest Research Institute

Prepared for:

Municipal Environmental Research Laboratory

December 1975

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

090014

PB 251 131

[illegible]

UNITED STATES ENVIRONMENTAL PROTECTION

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/2-75-041

2.

3. RECIPIENT'S ACCESSION NO.
PB251131

4. TITLE AND SUBTITLE
DETERMINATION OF INCINERATOR OPERATING CONDITIONS NECESSARY FOR SAFE DISPOSAL OF PESTICIDES

5. REPORT DATE
December 1975 (Issuing Date)

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Thomas L. Ferguson, Fred J. Bergman, Gary R. Cooper, Raymond T. Li, and Frank I. Honea

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

10. PROGRAM ELEMENT NO.
1DB311; ROAP 21BKV; Task 008

11. CONTRACT/~~GRANT~~ NO.
68-03-0286

12. SPONSORING AGENCY NAME AND ADDRESS
Municipal Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE
EPA-ORD

15. SUPPLEMENTARY NOTES
Project Officers: Donald A. Oberacker and Richard A. Carnes

16. ABSTRACT

An experimental incineration system was designed and constructed to evaluate the effect of operational variables (rate of pesticide injection, percent excess air, operating temperature, and retention time) on the efficiency with which organic pesticides can be incinerated. This system included a pilot-scale incinerator (45.4 kg/hr (100 lb/hr) Type 1 waste capacity), a three-stage scrubber, and a scrubber water treatment system. Nine pesticides in 15 liquid and solid formulations were tested by injection into the primary combustion chamber. The pesticides studied were DDT, aldrin, picloram, malathion, toxaphene, atrazine, captan, zineb, and mirex.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Detoxification Incinerators Pesticides Temperature Research	Residence time Incinerator conditions Pesticides destruction Time/temperature Surplus pesticides	13B

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS (This Report)
UNCLASSIFIED

20. SECURITY CLASS (This page)
UNCLASSIFIED

21. NO. OF PAGES
415

22. PRICE
$11.00

EPA Form 2220-1 (9-73)

*USGPO: 1976 — 657-695/5360 Region 5-11

EPA-600/2-75-041
December 1975

DETERMINATION OF INCINERATOR OPERATING CONDITIONS NECESSARY FOR SAFE DISPOSAL OF PESTICIDES

by

Thomas L. Ferguson, Fred J. Bergman,
Gary R. Cooper, Raymond T. Li, and Frank I. Honea
Midwest Research Institute
Kansas City, Missouri 64110

Contract No. 68-03-0286

Project Officers

Donald A. Oberacker and Richard A. Carnes
Solid and Hazardous Waste Research Division
Municipal Environmental Research Laboratory
Cincinnati, Ohio 45268

Copyright © National Technical
Information Service 1976

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

This report has been reviewed by the Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise, and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The Municipal Environmental Research Laboratory contributes to this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

Surplus and unwanted pesticide and pesticide containers pose safety hazards to the public and are potential sources of environmental contamination. In this study data have been developed that define the operating conditions needed for the safe disposal of organic pesticides by incineration.

Louis W. Lefke
Acting Director
Municipal Environmental
Research Laboratory

ABSTRACT

This research program was initiated with the overall objective of determining design and operational criteria for incinerators that can effect complete thermal degradation of pesticides.

An experimental incineration system was designed and constructed to evaluate the effect of operational variables (rate of pesticide injection, percent excess air, operating temperature, and retention time) on the efficiency with which organic pesticides can be incinerated. This system included a pilot-scale incinerator (45.4 kg/hr (100 lb/hr) Type 1 waste capacity), a three-stage scrubber, and a scrubber water treatment system. Nine pesticides in 15 liquid and solid formulations were tested by injection into the primary combustion chamber. The pesticides studied were DDT, aldrin, picloram, malathion, toxaphene, atrazine, captan, zineb, and mirex.

Results of the incineration test were evaluated in terms of the efficiency of active ingredient destruction, i.e., the percent of the pesticide destroyed. Efficiencies of greater than 99.99% were achieved for all pesticides tested except mirex over a range of combustion chamber retention time-temperature combinations. Test results were used to estimate stack emission rates for the subject pesticides when incinerated at 1000°C (1832°F) with 2 sec retention time.

A set of operating conditions (temperature, retention time, and excess air rate) was developed from comparable results for all 15 formulations which is believed to be applicable to the incineration of all organic pesticides.

Analysis of the incinerator effluents also showed that high concentrations of sulfur dioxide and cyanide were present when organosulfur and organonitrogen pesticides, respectively, were incinerated under certain operating conditions. Particulate loadings in the effluent gases during the incineration of solid pesticide formulations (dusts, wettable powders, granules, and pellets) were above federal limits established for new stationary sources having a capacity of or greater than 45,000 kg/day (50 tons/day). Thus, emission control devices will be required for pesticide incinerators.

Additional research is required before operating guidelines can be developed for the incineration of all organic pesticides and pesticide-containing solid wastes.

This report was submitted in fulfillment of Contract No. 68-03-0286 by Midwest Research Institute under the sponsorship of the Environmental Protection Agency. Work was completed as of 28 February 1975.

CONTENTS

Page

Disclaimer ii

Foreword iii

Abstract iv

List of Figures. vii

List of Tables xi

Acknowledgements xvii

Summary. 1

Sections

I Conclusions. 7

II Recommendations. 9

III Introduction 11

- Objectives and Scope 12
- Pesticide Selection. 14
- Report Organization. 14

IV Experimental Methods and Equipment 19

- Experimental Facilities. 20
- Sampling and Analysis. 25
- Experimental Design. 30

CONTENTS (Concluded)

Page

V Results 35

Specific Results. 36

DDT 36
Aldrin. 43
Picloram. 45
Malathion 51
Toxaphene 55
Atrazine. 59
Captan. 63
Zineb 65
Mirex 67

General Findings. 70
System Performance. 71
Problem Areas 71

VI Discussion. 73

Significance of Test Results. 79
Pesticide Incineration System Design Analysis . . . 79

Incinerator 79
Air Pollution Control Considerations. 80

Research Needs. 83

VII References. 85

Appendix A - Experimental Equipment 89

Appendix B - Test Results 113

Appendix C - Sampling and Analysis. 335

Appendix D - Calculations 389

FIGURES

No.	Title	Page
1	Experimental incineration system	21
2	Incinerator configuration	22
3	Solid pesticide formulation injection system	24
4	Scrubber system	26
5	Sample point, thermocouple, and manometer locations	27
6	Gas sampling train	29
7	Ranges of total species output ratios for the 15 formulations tests	74
8	Ranges of total species off-gas emissions for the 15 formulations tests	76
9	Estimated total species off-gas emission rates at 2 sec retention time and 1000°C	77
10	Time-temperature zones for pesticide incineration	78
11	Incinerator thermocouple locations	91
12	Liquid pesticide feed system - fuel oil miscible formulations	94
13	Diagram 0.6 to 3.0 gal/hr fuel oil burner	95
14	Diagram 3.0 to 8.0 gal/hr fuel oil burner	96
15	Liquid pesticide feed system - water based formulations	97

FIGURES (Continued)

No. Title Page

16 Modified injection nozzle 98

17 Solid formulation injection system. 100

18 Dust injection nozzle 101

19 Scrubber water treatment system 108

20 Representative chromatogram of 25% EC DDT formulation 123

21 DTA analysis of recrystallized aldrin 149

22 TGA analysis of recrystallized aldrin 150

23 DTA analysis of 19% aldrin granules 151

24 TGA analysis of 19% aldrin granules 152

25 Chromatogram of 41.2% aldrin EC formulation 155

26 DTA of picloram pellets 173

27 TGA of picloram pellets 174

28 DTA of recrystallized picloram. 175

29 TGA of recrystallized picloram. 176

30 Representative picloram chromatograms 179

31 Picloram pellets and residue. 193

32 Primary chamber residue sampler 196

33 DTA of malathion powder 206

34 TGA of malathion powder 207

35 DTA of malathion. 209

36 TGA of malathion. 210

FIGURES (Continued)

No.	Title	Page
37	DTA of technical toxaphene	229
38	TGA of technical toxaphene	230
39	DTA of ~ 20% toxaphene dust	231
40	TGA of ~ 20% toxaphene dust	232
41	DTA of recrystallized toxaphene	234
42	TGA of recrystallized toxaphene	235
43	Representative toxaphene chromatograms	237
44	Interior of plugged incinerator	249
45	DTA of technical atrazine	256
46	TGA of technical atrazine	257
47	DTA of dried liquid atrazine formulation	258
48	TGA of dried liquid atrazine formulation	259
49	DTA of ~ 80% atrazine wettable powder	260
50	TGA of ~ 80% atrazine wettable powder	261
51	Representative atrazine chromatograms	263
52	Liquid atrazine formulation injection system	267
53	DTA of technical captan	285
54	TGA of technical captan	286
55	DTA of a 50% captan wettable powder	287
56	TGA of 50% captan wettable powder	288
57	DTA of technical zineb	302

FIGURES (continued)

No.	Title	Page
58	TGA of technical zineb	303
59	DTA of 75% zineb wettable powder	304
60	TGA of 75% zineb wettable powder	305
61	Particulate discharge during zineb incineration	317
62	DTA of technical mirex	322
63	TGA of technical mirex	323
64	Gas sampling train	337
65	Particulate-sampling train	342
66	Particulate field data	345
67	Preliminary moisture determination data	349
68	Particulate clean-up and analysis data	350
69	Gas sampling train	355
70	SO_2 sampling train	363
71	Sampling train, flask valve, and flask	368
72	Moisture sampling train	375
73	Cyanide sampling train	384

TABLES

No.	Title	Page
1	Chemical structures of test pesticide	15
2	Classification of pesticides by chemical structure	16
3	Summary of test results--25% DDT EC formulations	39
4	Summary of test results--10% DDT dust formulations	42
5	Summary of test results--41.2% aldrin EC formulation	44
6	Summary of test results--19% aldrin granular formulation	46
7	Summary of test results--21.5% picloram liquid formulation	48
8	Summary of test results--10% picloram pellet formulation	50
9	Summary of test results--57% malathion EC formulation	53
10	Summary of test results--25% malathion WP formulation	54
11	Summary of test results--60% toxaphene EC formulation	57
12	Summary of test results--20% toxaphene dust formulation	58

TABLES (continued)

No.	Title	Page
13	Summary of test results--4 lb/gal atrazine liquid formulation	61
14	Summary of test results--80% atrazine WP formulation .	62
15	Summary of test results--50% captan WP formulation . .	64
16	Summary of test results--75% zineb WP formulation . . .	66
17	Summary of test results--0.3% mirex bait formulation .	69
18	Design data for pesticide incineration	81
19	Scrubber types and applications	83
20	Incinerator design parameters	93
21	Design of scrubbing system	102
22	Ancillary equipment	110
23	Factorial design for 25% DDT EC experiments	125
24	Summary of 25% DDT EC experiments	127
25	Incinerator efficiency--25% DDT EC formulation	128
26	Off-Gas composition--25% DDT EC liquid incineration . .	129
27	Operational data summary--25% DDT EC experiments . . .	130
28	Summary of 10% DDT dust experiments	137
29	Residue and off-gas characteristics--10% DDT dust experiments	138
30	Off-Gas composition--10% DDT dust incineration	139

TABLES (continued)

No.	Title	Page
31	Particulate sampling summary--10% DDT dust experiments	140
32	Operational data summary--10% DDT dust experiments . .	141
33	Summary of 41.2% aldrin EC experiments	157
34	Incineration efficiency--41.2% aldrin EC formulation .	158
35	Off-Gas composition--41.2% aldrin EC incineration . . .	159
36	Operational data summary--41.2% aldrin EC experiment .	160
37	Summary of 19% aldrin granule experiments	162
38	Residue and off-gas characteristics--19% aldrin granule experiments	163
39	Off-Gas composition--19% aldrin granule incineration .	164
40	Particulate sampling summary--19% aldrin granule experiments	165
41	Operational data summary--19% aldrin granule experiments	166
42	Summary of 21.5% picloram liquid experiments	182
43	Incineration efficiency--21.5% picloram liquid formulation	183
44	Off-gas composition--21.5% picloram liquid incineration	184
45	Operational data summary--21.5% picloram liquid experiments	185
46	Summary of 10% picloram pellet experiments	188
47	Residue and off-gas characteristics--10% picloram pellet experiments	189

TABLES (continued)

No.	Title	Page
48	Off-gas composition--10% picloram pellet incineration	190
49	Particulate sampling summary--10% picloram pellet experiments	191
50	Operational data summary--10% picloram pellet experiments	192
51	Summary of 57% malathion EC experiments	213
52	Incineration efficiency--57% malathion EC experiments	214
53	Off-gas composition--57% malathion EC incineration	215
54	Operational data summary--57% malathion EC experiments	216
55	Summary of 25% malathion wettable powder experiments	218
56	Residue and off-gas characteristics--25% malathion wettable powder experiments	219
57	Off-gas composition--25% malathion dust incineration	220
58	Particulate sampling summary--25% malathion wettable powder experiments	221
59	Operational data summary--25% malathion wettable powder experiments	222
60	Summary of 60% toxaphene EC experiments	239
61	Off-gas composition--60% toxaphene EC incineration	240
62	Operational data summary--60% toxaphene EC experiments	241
63	Summary of 20% toxaphene dust experiments	243

TABLES (continued)

No.	Title	Page
64	Residue and off-gas characteristics--20% toxaphene dust experiments	244
65	Off-gas composition--20% toxaphene dust incineration	245
66	Particulate sampling summary--20% toxaphene dust experiments	246
67	Operational data summary--60% toxaphene dust experiments	247
68	Summary of 40.8% atrazine flowable concentrate experiments	268
69	Incineration efficiency--40.8% atrazine flowable concentration experiments	269
70	Off-Gas composition--40.8% atrazine flowable concentrate incineration	270
71	Operational data summary--40.8% atrazine flowable concentrate experiments	271
72	Summary of 80% atrazine wettable powder experiments	272
73	Residue and off-gas characteristics--80% atrazine wettable powder incineration	273
74	Off-Gas composition--80% atrazine wettable powder incineration	274
75	Particulate sampling summary--80% atrazine wettable powder experiments	275
76	Operational data summary--80% atrazine wettable powder experiments	276
77	Summary of 50% captan wettable powder experiments	291

TABLES (concluded)

No.	Title	Page
78	Incineration efficiency--50% captan wettable powder experiments	292
79	Off-gas composition--50% captan wettable powder incineration	293
80	Particulate sampling summary--50% captan wettable powder experiments	294
81	Operational data summary--50% captan wettable powder experiments	295
82	Summary of 75% zineb wettable powder experiments	310
83	Residue characteristics--75% zineb wettable powder experiments	311
84	Off-gas composition--75% zineb wettable powder incineration	312
85	Operational data summary--75% zineb wettable powder experiments	313
86	Particulate sampling summary--75% zineb wettable powder experiments	314
87	Summary of 0.3% mirex bait experiments	326
88	Residue and off-gas characteristics--0.3% mirex bait experiments	327
89	Off-gas composition--0.3% mirex bait experiments	328
90	Operational data summary--0.3% mirex bait experiments	329
91	Particulate sampling summary--0.3% mirex bait experiments	331
92	Solvent selection	339

ACKNOWLEDGEMENTS

This report presents the results of a study of the pilot-scale incineration of pesticides conducted by Midwest Research Institute, under EPA Contract No. 68-03-0286, MRI Project No. 3813-C. The work was performed in the Physical Sciences Division of Midwest Research Institute, Dr. H. M. Hubbard, Director. Dr. Larry J. Shannon, Head of the Environmental Systems Section, Physical Sciences Division, was administratively responsible for this program. This report was written by Mr. Thomas L. Ferguson and Mr. Fred J. Bergman (Principal Investigators), Mr. Gary G. Cooper, Dr. Raymond T. Li, and Dr. Frank I. Honea.

Project officers for the Environmental Protection Agency were Messrs. Donald A. Oberacker and Richard A. Carnes.

SUMMARY

The problem of how to dispose of unwanted pesticides and pesticide-containing solid waste has been recognized for some time. Only recently, however, has the development of environmentally acceptable methods of disposal for these materials been fully addressed. The U.S. Environmental Protection Agency (EPA), under authority of the "Federal Insecticide, Fungicide, and Rodenticide Act" as amended by the "Federal Environmental Pesticide Control Act of 1972," has recommended procedures for the disposal and storage of pesticides and pesticide containers. The procedure recommended for the disposal of organic pesticides is incineration at a temperature of 1000°C (1832°F) for 2 sec retention time, or at other temperature-retention time combinations that effect complete destruction of the pesticide. The available data on pesticide incineration, however, are not sufficient to determine specific operating guidelines for full-scale incineration of unwanted organic pesticides and pesticide containers.

This research study was initiated with the overall objective of determining design and operational criteria for the incineration of pesticides, combustible pesticide containers, and washings from pesticide containers. Efforts were focused on the development of combustion data for a number of representative pesticides (active ingredients). An experimental pilot-scale incineration system (45.4 kg/hr (100 lb/hr) Type 1 waste* capacity) was designed and constructed to evaluate the effect of

---

* Type 1 waste is defined as rubbish, a mixture of combustible waste such as paper, cardboard cartons, wood scrap, foliage and combustible floor sweepings, from domestic, commercial and industrial activities. This type of waste contains 25% moisture, 10% incombustible solids and has a heating value of 1.51×10^7 J/kg (6,500 Btu/lb).

operating variables (pesticide injection rate, operating temperature, retention time, turbulence, and excess air rate) on the efficiency of pesticide destruction. Injection nozzles were provided in the primary combustion chamber for both liquid and solid pesticide formulations.

Nine representative active ingredients were selected for study by EPA from the major classes of organic pesticides, i.e., chlorinated organic, organophosphate, organonitrogen, and organosulfur. These pesticides (DDT, aldrin, picloram, malathion, toxaphene, atrazine, captan, zineb, and mirex) were tested using 15 commercial formulations, including emulsifiable concentrates, wettable powders, dusts, a granule, a pellet, and a bait.

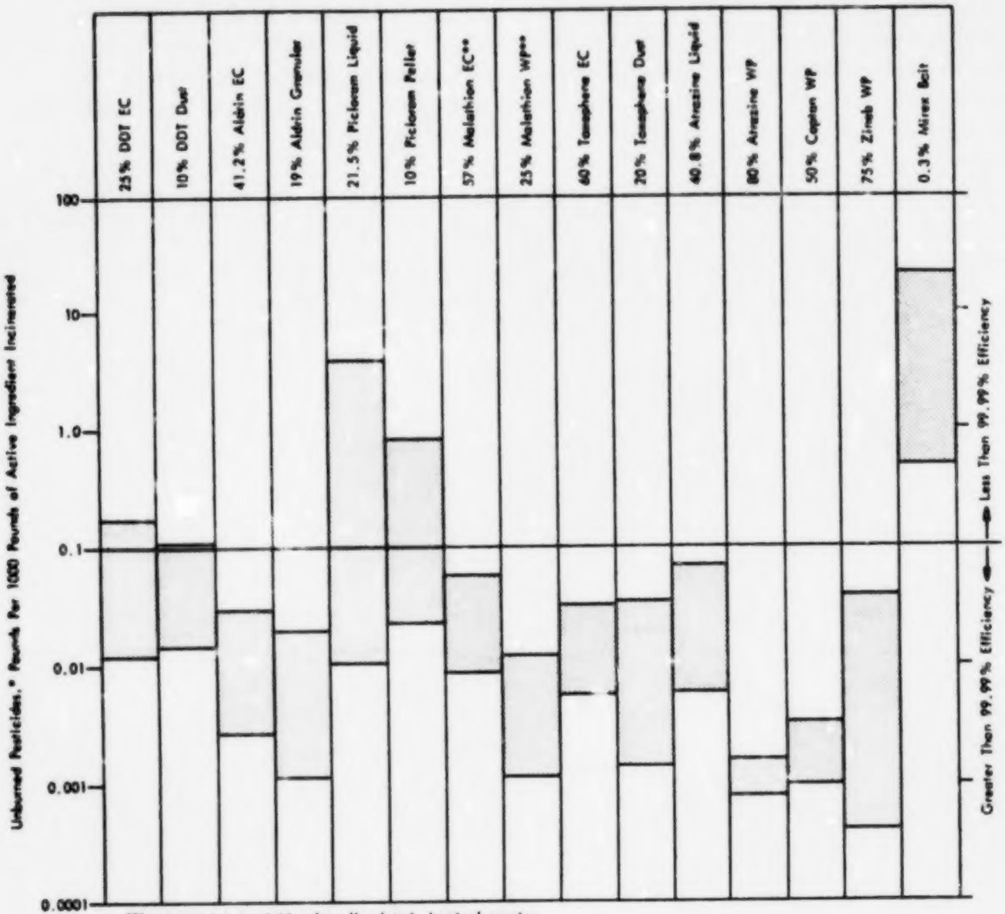
Major emphasis was given to quantification of the active ingredient (plus all closely related partially degraded chemical species) not destroyed by the incineration process. To this end, nine sample points were established in the experimental apparatus.

The measure of performance that has been used to evaluate test results is the efficiency to which the active ingredient was decomposed within the incinerator during a period of steady state operation. This efficiency, expressed as a percentage, equals $\left[1 - \frac{\text{Quantity } \underline{\text{out}}}{\text{Quantity } \underline{\text{in}}}\right] \times 100$. The Quantity in (the amount of active ingredient fed into the incinerator) has been determined by volumetric measurement and quantitative analysis of the pesticide-containing mixture injected into the incinerator. Representative samples of the undiluted incinerator off-gas were analyzed and, in combination with a determination of the total volume of undiluted gas, were used to determine the amount of pesticide in the effluent gas. Analogous determinations were made for any solid residue left in the incinerator, e.g., from tests involving dust, wettable powder, pellet, bait, or granular formulations. The amount of active ingredient plus related chemical species remaining in the incinerator off-gas and solid residues was defined as the Quantity out. For DDT as an example, the Quantity out included DDT* plus all other chlorinated hydrocarbons detected.

---

* "DDT" has been defined to include four major isomers commonly found in the technical material, i.e., p,p'-DDT, o,p'-DDT, p,p'-DDE, and o,p'-DDE.

The efficiency of pesticide incineration was generally uniformly high over the complete ranges of operating variables investigated. The only exception was the 0.3% mirex bait formulation. The range of results for each formulation, expressed as pounds of the respective pesticide plus all related chemical species detected in the incinerator off-gas and solid residues per 1,000 lb of active ingredient incinerated, were as follows:

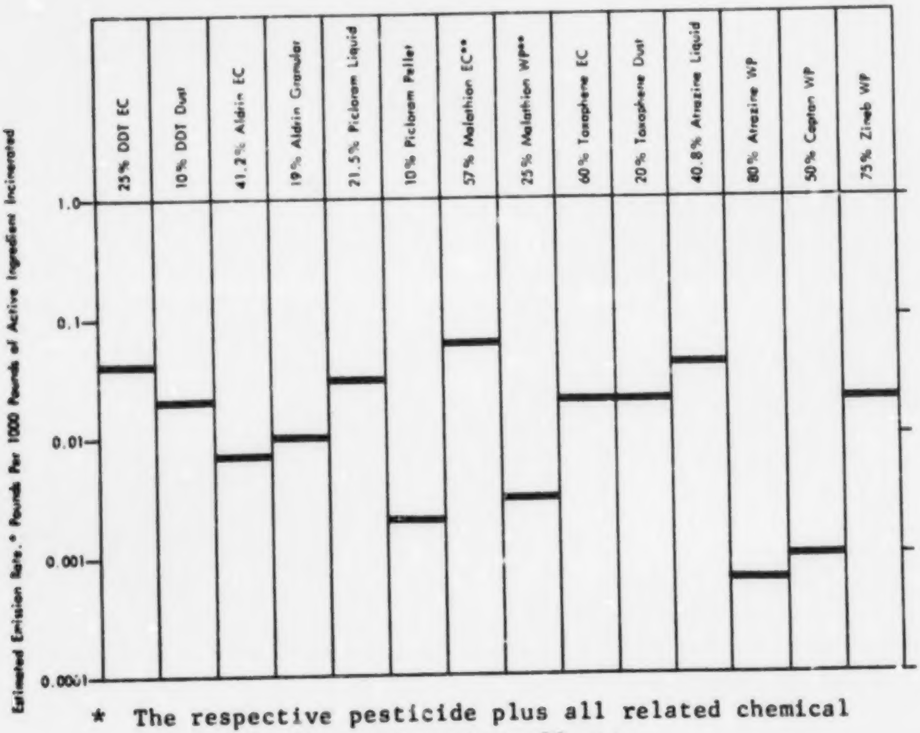


*The respective pesticide plus all related chemical species detected in the incinerator off gas and solid residues.

**Based on Malathion detection limit.

The ranges reported for the two malathion formulations are not strictly comparable to the other results because they are calculated from analytical detection limits for malathion (no malathion was detected in the effluent from most tests) rather than from actual emission data.

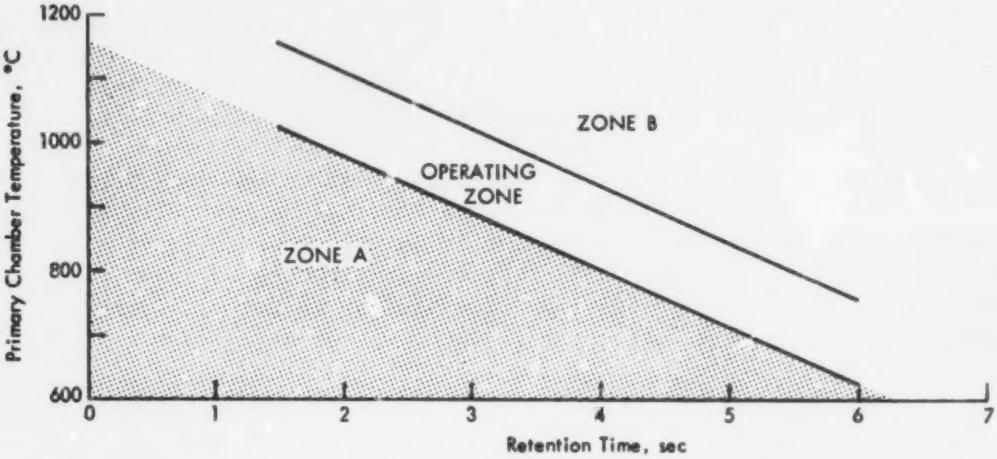
The test data indicate that most organic pesticides can be destroyed (i.e., greater than 99.99% of the active ingredient destroyed) over a range of retention time-temperature combinations. Estimates were made of the emissions (active ingredient plus related chemical species) in the incinerator off-gas when the subject pesticides are incinerated at 2-sec retention at 1000°C (1832°F). (The 0.3% mirex formulation was excluded from this analysis because of the limited data in the time-temperature area of interest.) These estimates, again expressed as pounds of active ingredient plus related chemical species per 1,000 lb of active ingredient incinerated, are as follows:



* The respective pesticide plus all related chemical species in the incinerator off-gas.

** Based on malathion detection limit.

An evaluation was also made of comparable results for all 15 formulations tested in an attempt to hypothesize operating conditions (retention time-temperature combinations) generally applicable to the incineration of organic pesticides when similarly injected. The result of this evaluation is shown in the following diagram:



Zone A represents operating conditions at which less than 99.99% efficiency may result, the Operating Zone represents conditions at which efficiencies of at least 99.99% are expected, and Zone B represents conditions at which greater than 99.99% are anticipated. The acceptable range for excess air is estimated to be 80 to 160%.

Samples of solid formulations removed from the combustion chamber after about 2-sec residence were found to contain significant levels of pesticide. Approximately 10 and 30% of the active ingredient in 10% picloram pellets and 0.3% mirex bait, respectively, was still present. These findings demonstrate (a) the need to insure adequate retention of solid residues in the combustion chamber, and (b) the inadequacy of conventional retention time calculations (based on the volume of off-gas) in defining solid residue retention time.

The stack gases from all incineration tests were also analyzed for SO_2, NO_x, CO, CO_2, CH_4, total hydrocarbons, and for particulate emissions. In addition, analyses were conducted for cyanide (as CN^-) and total pyrophosphates when organonitrogen and organophosphate pesticides, respectively, were tested.

The organonitrogen pesticides generated measurable quantities of cyanide (CN^-) at the temperatures tested (640 to 1040°C). The cyanide concentration of the incinerator off-gas, however, could generally be controlled by increasing the operating temperature and percent excess air above that required for pesticide destruction (greater than 99.99% degradation).

Particulate loadings in the effluent gases during the incineration of solid pesticide formulations (dusts, wettable powders, granules, and pellets) were above federal limits established for new stationary sources having a capacity of or greater than 45,000 kg/day (50 tons/day).

The results of these tests show that emission control devices will be required for pesticide incineration. Emissions potentially requiring control include particulates from solid formulations, P_2O_5 from phosphorus-based pesticides, HCl from chlorinated hydrocarbons, CN^- from nitrogen-containing organics, and SO_2 from organosulfur compounds. Odor is also a problem, particularly during the incineration of organosulfur pesticides.

Additional research is required in three areas before operating guidelines applicable to all organic pesticides as well as pesticide-containing solid waste can be developed. These include (a) work at the pilot scale to determine necessary combustion conditions for additional representative pesticides and for pesticide-containing solid wastes, (b) verification or revision of the generalized time-temperature-excess air guidelines, utilizing the additional data, and (c) further characterization of the effluents from pesticide incineration in order to specify adequate emission devices.

SECTION I

CONCLUSIONS

The following conclusions have been drawn from this study of the incineration of pesticides.

1. Most organic pesticides can be destroyed, i.e., > 99.99% of the active ingredient degraded, by incineration.

2. A range of retention time-temperatures exists at which these pesticides can be > 99.99% destroyed.

3. The two most important operating variables are temperature and retention time (dwell time) in the combustion chamber.

4. Conventional waste incinerators having adequate retention time and operating temperature are potential facilities for pesticide incineration using the injection methods described herein. However, modifications would probably be required because of the corrosive nature of the effluent gas from pesticide incineration and the need for emission control devices.

5. Incineration of organonitrogen pesticides at the temperatures tested (640 to 1040°C) generates measurable quantities of cyanide (CN^-). The cyanide concentration of the incinerator off-gas can generally be controlled by increasing the operating temperature and percent excess air above that required for pesticide destruction (> 99.99% degradation).

6. Emission control devices will be required for pesticide incineration. Emissions potentially requiring control include particulates from solid formulations, P_2O_5 from phosphorus-based pesticides, HCl from chlorinated hydrocarbons, CN^- from nitrogen-containing organics, and SO_2.

7. The solid residues left from the incineration of only pesticide formulations generally contain very low levels of the pesticide, e.g., < 20 ppm.

8. Odor is a potential operational problem for pesticide incineration, particularly during the destruction of organosulfur pesticides.

SECTION II

RECOMMENDATIONS

The feasibility for the destruction of unwanted organic pesticides by incineration at the pilot scale has been demonstrated. There are several areas, however, in which further study is needed. Recommended activities include:

1. Development of operating condition data for the incineration of additional representative pesticides and pesticide formulations.

2. Full-scale testing of representative pesticide incineration in order to confirm the design and operational guidelines that have been developed and to test their scale-up.

3. Pilot-scale testing of the incineration of pesticide-containing solid wastes.

4. Development of guidelines for the incineration of pesticide-containing solid wastes based on the above pilot-scale investigation and confirmation by a limited number of large-scale tests.

5. Pilot-scale investigation of the "bake-out" principle of pesticide incineration, i.e., the combustion of bulk pesticides (bags, cartons, etc.) using a long retention time in the combustion chamber, as a possible alternative to particulate emissions control, and the effect of longer test periods on the pesticide content of solid residues.

6. Investigation of particulate control devices for use during solid pesticide formulation incineration.

7. Determination of the physical state and properties, i.e., particle size distribution of the pesticide-containing particulate emissions in order to better assess their environmental significance.

8. Investigation of pesticide and pesticide-containing solid waste feeding systems for pesticide incineration.

9. Investigation of solid residue removal and handling methods for pesticide incineration.

10. Development of improved analytical techniques to determine the composition of incinerator emissions for the specific pesticides tested.

11. Additional investigations of the chemical species generated, i.e., partial degraded pesticides, from pesticide incineration.

12. Characterization of the scope and geographic distribution of the pesticide disposal problem.

SECTION III

INTRODUCTION

The problem of how to dispose of unwanted pesticides and pesticide containers has been recognized for several years.[1,2] The development of environmentally acceptable methods for disposal of these materials, however, has not been fully addressed until rather recently.[3,4] Pesticides improperly disposed of, even in small quantities, may damage the local environment or pose a hazard to individuals. Large quantities of improperly disposed of pesticides would have undesirable local impact as well as add to global environmental pollution.

The "Federal Insecticide, Fungicide, and Rodenticide Act," as amended by the "Federal Environmental Pesticide Control Act of 1972,"[5] requires the Administrator of the U.S. Environmental Protection Agency to establish regulations and procedures for the disposal and storage of pesticides and pesticide containers. However, adequate disposal sites and facilities are not readily available nationwide, and significant information gaps exist which make it infeasible to write specific criteria for disposal methods and procedures. Alternatively, the Agency has issued recommended procedures for the disposal and storage of pesticides and pesticide containers.[6,7]

The recommended procedure for organic pesticide disposal is incineration at a temperature of 1000°C (1832°F) for 2 sec retention (dwell) time in the combustion zone, or at other temperature-retention time combinations that effect complete destruction of the pesticide.

The thermal degradation of pesticides, i.e., conversion of the pesticide to other organic and inorganic substances by heating in an oxygen-sufficient (combustion) or oxygen-deficient (pyrolysis) atmosphere, has been the subject of several research studies. Hanneman and Porter[8] demonstrated that certain dithiophosphates could be pyrolyzed at ≥ 215°C to form volatile olefins structurally related to the alkyl group in the original phosphate compound. Anthony and Shuman[9] have shown that malathion can be successfully incinerated in a specially designed model incinerator.

Studies by Putnam et al.[10] have shown that, in gram quantities, many pesticides can be destroyed (99% combustion) by open burning in a flattened polyethylene bag surrounded by other combustible materials. While oxidizing agents and binders were found to aid destruction, the combination of oxidants and binders was found to be no more effective than binders alone.

The incineration of DDT in a kerosene carrier has been studied by Whaley et al.[11] at the Canadian Combustion Research Laboratories in Ottawa. Their work has shown that a DDT-kerosene formulation can be destroyed in an incinerator utilizing a commercially available blue-flame burner. This study provided the design data from which the Canadian Department of National Defence built and operated a special incineration system to destroy 107,000 gal. of a DDT-kerosene formulation. Further study by Lee et al.[12] has shown that a DDT dust formulation can be similarly destroyed.

Thermal degradation of pesticides also has been studied at the laboratory scale by several investigators at Mississippi State University.[13-18] Their results indicate that the minimum temperature required for complete incineration is dependent on the specific pesticide, and can range from 250°C to more than 600°C.[13]

These earlier studies, however, failed to yield sufficient data to determine design and operation guidelines for full-scale incineration of unwanted pesticides and pesticide containers. The subject study was initiated in order to develop these data.

OBJECTIVES AND SCOPE

This research program was initiated with the overall objective of determining design and operational criteria for incinerators that can effect complete thermal degradation of pesticides, combustible pesticide containers, and washings from containers.

Specific objectives to be accomplished during the program were:

1. Determination of optimum combustion conditions for selected pesticide formulations in a pilot scale incinerator. Representatives of four major classes of pesticides (organochlorine, phosphorus, nitrogen, and sulphur) were to be investigated.

2. Determination of the effect of selected materials on combustion of pesticides. The materials were to include combustible container materials, sewage sludge, municipal refuse, waste industrial liquids, and liquids used to clean noncombustible pesticide containers.

3. Development of guidelines for design and use of incinerators for pesticide destruction. The guidelines were to encompass conventional incinerators as well as new incinerators designed specifically to handle pesticides.

Work was initiated toward these objectives using a three phase research plan.

Phase I was the determination of incinerator operating conditions which would most effectively degrade specific pesticides. It was planned that representative pesticides (one from each of four major chemical classes--chlorinated organic, organophosphate, organonitrogen, and organosulfur) would be extensively investigated in statistically designed tests to determine their respective optimum incineration conditions.

Phase II was the determination of the effect of other waste materials on the efficiencies of incineration for the four representative pesticides obtained in Phase I.

The third and final phase under the original research plan was the development of guidelines for the design and selection of pesticide incinerators. Using the results from the two initial phases, minimum values for operating conditions necessary to achieve complete destruction of the specific pesticides were to be established. These conditions were then to be used in developing guidelines for determining the suitability of existing incinerators and conventional municipal incinerator design parameters for pesticide disposal.

However, only one pesticide (DDT) was studied using these initial objectives and research plan. After completion of the DDT experiments, efforts were focused on the development of combustion data for a number of pesticides. Included in the pesticides studied were those representing acute disposal problems because of actual or potential registration cancellation, and those representative of various chemical classes of pesticides.

The modified research plan used for the remainder of the program included a two-phased study of each pesticide. First, preliminary thermal analyses (differential thermal analysis (DTA) and thermal gravimetric analysis (TGA)) were conducted to identify temperatures at which the respective pesticides could be expected to decompose. Following this identification, a limited number of experiments were made within the favorable temperature range in order to determine the completeness of destruction that could be achieved.

PESTICIDE SELECTION

The pesticides studied during this research program were: DDT, aldrin, malathion, picloram, toxaphene, atrazine, captan, zineb, and mirex (see Table 1). The classification of these pesticides by chemical structure is given in Table 2.

DDT was the first pesticide studied and the only one extensively investigated. The combustion of DDT, a pesticide that currently represents an acute disposal problem, has been the subject of several other research studies. The experiment with DDT, then, not only provided data on its combustion, but also provided a means for relating our findings to those from other programs.

The eight additional pesticides were subsequently selected by EPA based on the suggestions of the Office of Solid Waste Management Programs (OSWMP) and Midwest Research Institute (MRI), as well as other divisions of EPA.

REPORT ORGANIZATION

The following subsections of this report (Sections IV through VII and Appendices A through D) give the results of the experiments conducted with the nine pesticides.

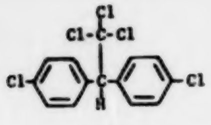
Section IV - Experimental Methods and Equipment, briefly describes the experimental facilities, methods of sampling and analysis, and experimental design used during the study. Complete detail of the facilities design is given in Appendix A, while details of sampling and standard analytical methods are given in Appendix C.

Section V - Results, briefly summarizes the experimental results, general findings, and problem areas from the experimental phase of the study. Detailed test results are presented in Appendix B. The last appendix to the report (Appendix D) gives details of calculation methods used to derive the results reported in Section V.

Section VI - Discussion, includes an overall discussion of the significance of the study as well as a brief analysis of system requirements for pesticide incineration.

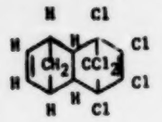
The final section of the report (Section VII) contains a listing of all references cited in the text. (References pertaining to the specific pesticides tested have been cited in the appropriate subsections of Appendix B.)

Table 1. CHEMICAL STRUCTURES OF TEST PESTICIDES

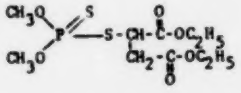


DDT

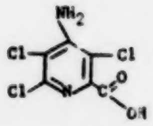
(A mixture of p,p'-isomers (75 to 80%), o,p'-isomers (15 to 20%), as well as related chlorinated compounds.)



ALDRIN

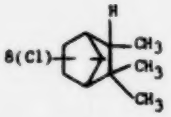


MALATHION



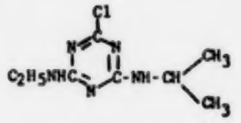
PICLORAM

(Tested as the potassium salt.)

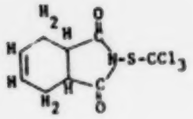


TOXAPHENE

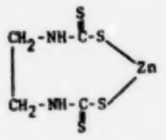
(Mixed isomers of chlorinated camphene, 67 to 69% chlorine.)



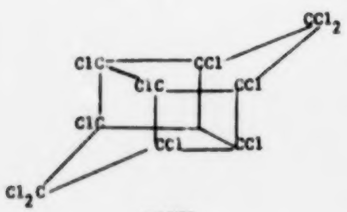
ATRAZINE



CAPTAN



ZINEB



MIREX

Table 2. CLASSIFICATION OF PESTICIDES BY CHEMICAL STRUCTURE[4]

Classification	Pesticides tested
Inorganic and Metallo-Organic Pesticides	
Mercury Compounds	
Arsenic Compounds	
Copper Compounds	
Other Heavy-Metal Compounds	
Cyanides, Phosphides and Related Compounds	
Other Inorganic Compounds	
Phosphorus-Containing Pesticides	
Phosphates and Phosphonates	
Phosphorothioates and Phosphonothioates	
Phosphorodithioates and Phosphonodithioates	Malathion
Phosphorus-Nitrogen Compounds	
Other Phosphorus Compounds	
Nitrogen-Containing Pesticides	
Carbamates and Related Compounds	
Thiocarbamates	
Dithiocarbamates[a]	Zineb
Anilides	
Imides and Hydrazides	Captan
Amides	
Ureas and Uracils	
Triazines	Atrazine
Amines, Heterocyclic (without sulfur)	Picloram
Amines, Heterocyclic (sulfur-containing)	
Nitro Compounds	
Quaternary Ammonium Compounds	
Other Nitrogen-Containing Compounds	

Table 2. (concluded)

Classification	Pesticides tested
Halogen-Containing Pesticides	
DDT	DDT
DDT Relatives	
Chlorophenoxy Compounds	
Aldrin-Toxaphene Group	Aldrin, Toxaphene, Mirex
Aliphatic and Alicyclic Chlorinated Hydrocarbons	
Aliphatic Brominated Hydrocarbons	
Dihaloaromatic Compounds	
Highly Halogenated Aromatic Compounds	
Other Chlorinated Compounds	
Sulfur-Containing Pesticides	
Sulfides, Sulfoxides and Sulfones	
Sulfites and Xanthates	
Sulfonic Acids and Derivatives	
Thiocyanates	
Other Sulfur-Containing Compounds	
Botanical and Microbiological Pesticides	
Organic Pesticides, Not Elsewhere Classified	
Carbon Compounds (< 9 carbon atoms)	
Carbon Compounds (> 9 carbon atoms)	
Anticoagulants	

---

a/ Ten of the 13 pesticides in this category (including zineb) would be classed as matallo-organic according to EPA disposal procedures.[6,7]

SECTION IV

EXPERIMENTAL METHODS AND EQUIPMENT

The selection of experimental methods and facilities used during this study was based on the initial objectives and scope as have been outlined above. At the inception of the project, it was decided that maximum flexibility be provided in the experimental system in order that no mechanical restraints prevent the determination of optimum incinerator operating conditions. For this reason, a commercial incineration unit was not used. Rather, a two-chambered experimental incinerator of pilot scale (i.e., 45.4 kg/hr (100 lb/hr) of Type 1 waste* capacity) was constructed and used. The secondary combustion chamber of the experimental incinerator was designed following Incinerator Institute of America (IIA) standards and constructed as a permanent installation.19/ The primary chamber was constructed of insulating firebrick layered up with mortar. This system was designed to allow for rapid changes in geometry (turbulence) and length (retention time) with a minimum of effort and lost time.

The following three subsections (Experimental Facilities, Sampling and Analysis, and Experimental Design) briefly describe the facilities and methods used to study the effects of incinerator operating conditions on the efficiency with which selected pesticides could be destroyed.

---

* Type I waste is defined as rubbish, a mixture of combustible waste such as paper, cardboard cartons, wood scrap, foliage and combustible floor sweepings, from domestic, commercial and industrial activities. The mixture contains up to 20% by weight of restaurant or cafeteria waste, but contains little or no treated papers, plastic or rubber wastes.

This type of waste contains 25% moisture, 10% incombustible solids and has a heating value of 1.51×10^7 J/kg (6,500 Btu/lb) as fired. Thus, the design capacity of the pilot scale incinerator was 6.86×10^8 J/hr (650,000 Btu/hr).

Preceding page blank

EXPERIMENTAL FACILITIES

An overall schematic of the experimental apparatus used is given in Figure 1. The experimental incinerator was located on a concrete pad immediately adjacent to a laboratory building which housed the three-stage scrubber system. The entire facility was located at MRI's Deramus Field Station which is used for research projects involving potentially hazardous materials or operations.

The following discussion summarizes the major characteristics of the experimental apparatus. Complete information on the system has been included as Appendix A.

Incinerator

The pilot-scale incinerator was constructed of standard (Morex®) firebrick using IIA design standards for a 45.4 kg/hr (100 lb/hr) Type 1 waste incinerator.[19] An outer shell was constructed using concrete blocks, and the void between the firebrick and concrete walls was filled with perlite. The primary chamber was initially provided with both front (primary) and side (alternate) burner positions, as shown in Figure 2.

Pesticide Injection Systems

Separate injection systems were provided for liquid and solid formulations. In addition, modification of the initial liquid formulation injection system was made in order to accommodate water-based formulations not compatible (miscible) with fuel oil. The liquid injection system, the modified liquid injection system, and the solid formulation injection system are briefly described as follows, while detailed information is given in Appendix A.

Solid Formulations

All solid pesticide formulations tested were injected through a system similar to that used for earlier studies of DDT dust incineration.[12]

The formulation was metered at a uniform rate by a variable speed vibrating screw feeder and fed into a stream of compressed air which injected the pesticide into the primary chamber of the incinerator through a water-cooled injection nozzle. The dust injection nozzle and the fuel oil burner were positioned in the primary burner position so that the flame and dust stream impinged on a horizontal plane at an angle of 30 degrees, and at a point approximately 8 cm (3 in.) from the front wall

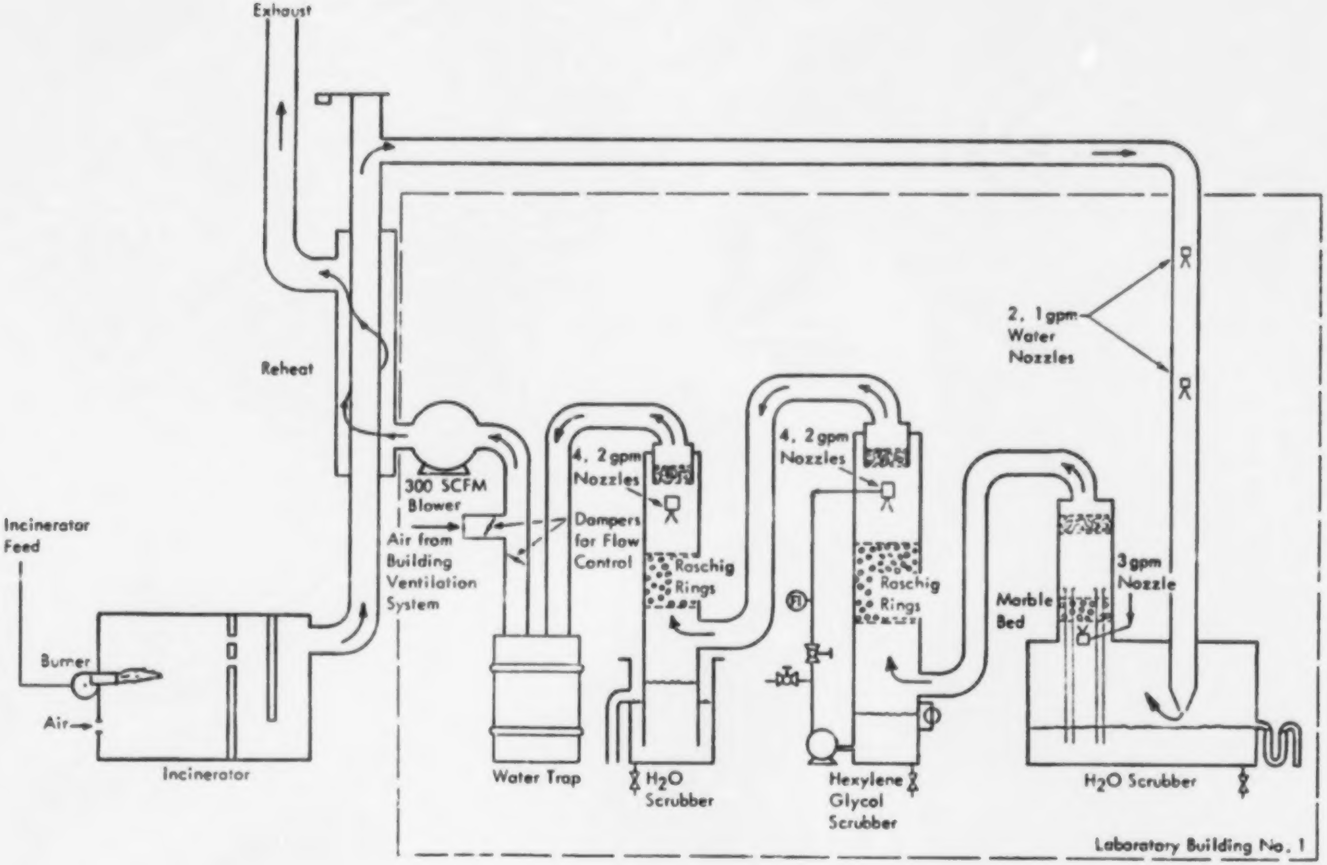


Figure 1. Experimental incineration system

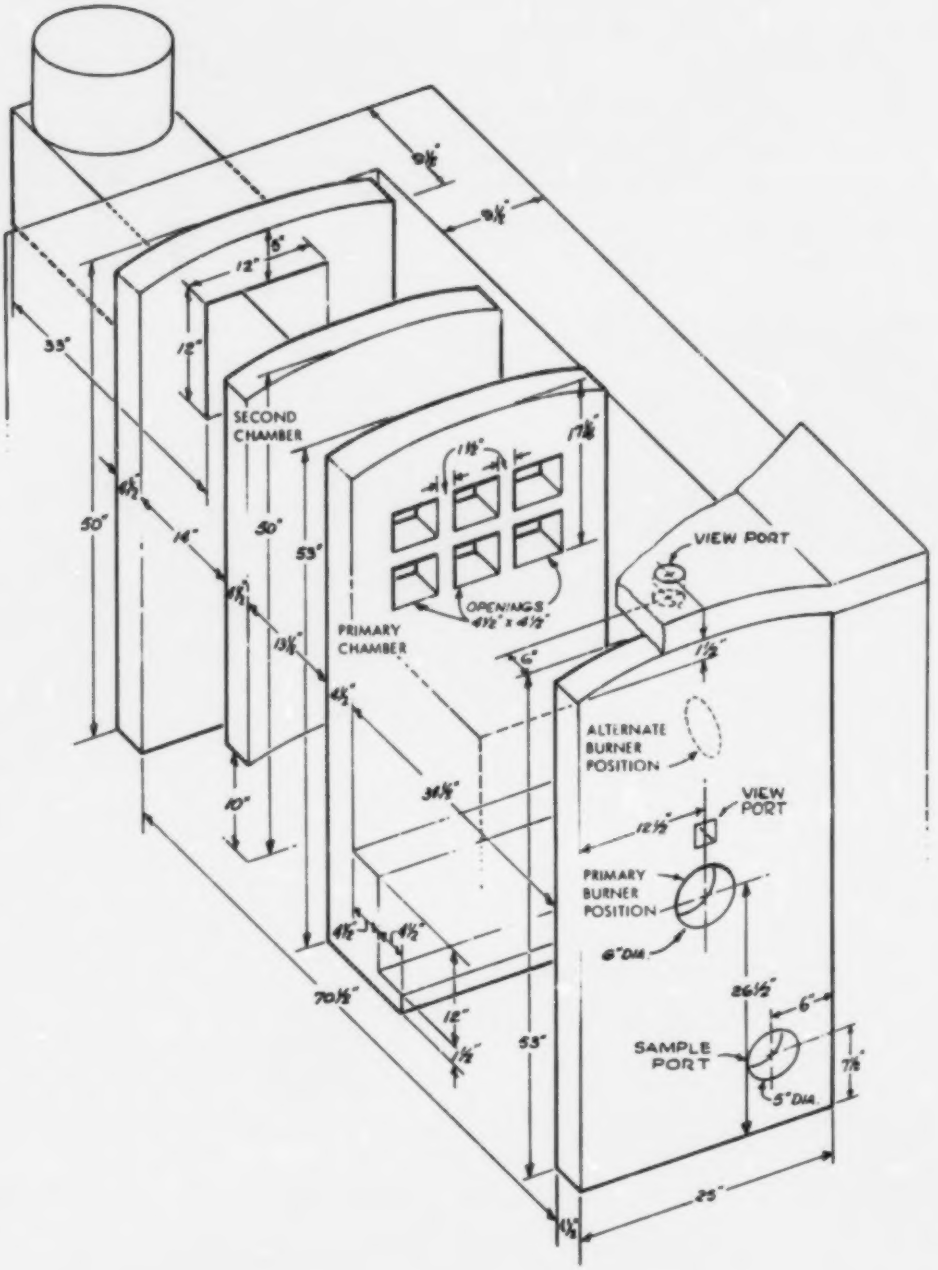


Figure 2. Incinerator configuration

of the primary chamber. A picture of the dust injection system in this configuration is shown in Figure 3. (See also Figure 17, p. 100).

An alternate configuration was used during the DDT experiments, where the oil burner was located in the primary burner position, and the pesticide injection nozzle was located in the alternate (side) burner position (see Figure 2). Thus, the flame and pesticide stream impinged at 90 degrees on a horizontal plane at the geometric center of the primary chamber.

Liquid Injection System

All liquid pesticide formulations miscible with No. 2 fuel oil were injected as pesticide fuel oil mixtures using standard fuel oil burners. The mixtures were gravity fed from batch holding tanks at a height of 2.4 m (8 ft) above the burner nozzle. Two burners with design capacities of 11.3 to 30.3 liters/hr (3 to 8 gal/hr), and 2.3 to 11.3 liters/hr (0.6 to 3 gal/hr), respectively, were used to inject the pesticide-fuel oil mixtures at the desired rate through the two burner positions provided in the primary chamber (see Figure 12, p. 94).

Modified Liquid Injection System

For those liquid formulations not compatible with No. 2 fuel oil, a dual injection system was used. Supplemental fuel (No. 2 fuel oil) was injected at the desired rate using the standard fuel oil burner equipped with the appropriately sized nozzle. The liquid formulation was pumped into the incinerator through a fuel oil nozzle of the same type being used in the oil burner. The liquid formulation and fuel oil were both fed to the respective pumps by gravity from batch holding tanks located 2.4 m (8 ft) above the injection nozzles.

The two injection systems were positioned in the primary burner position (see Figure 2) so that the liquid formulation and the flame from the fuel oil burner impinged on a horizontal plane at an angle of 30 degrees and at a point about 8 cm (3 in.) from the front wall of the primary chamber. This configuration, as described above, is the same used for injection of solid formulations (see Figure 15, p. 97).

A further modification was made to prevent plugging of the pesticide injection nozzle. This consisted of using the dust injection nozzle water jacket to cool the pesticide injection nozzle. (See Figure 16, p. 98.)

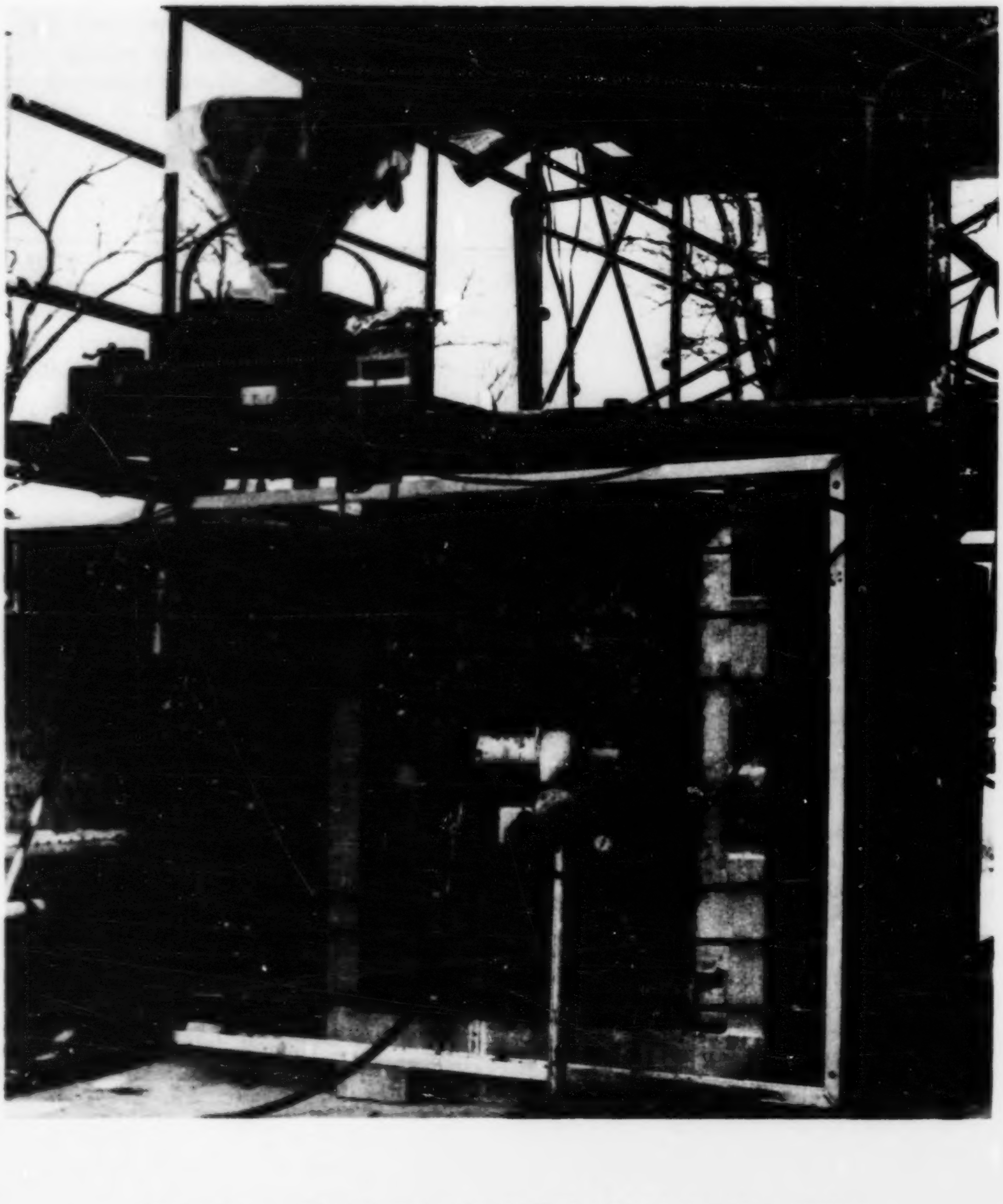


Figure 3. Solid pesticide formulation injection system

Scrubber System

A three-stage system was installed to scrub the incinerator off-gas prior to discharge to the atmosphere (see Figure 1). Water, hexylene glycol, and water, respectively, were used as the scrubber liquids. Scrubber waters from the first and third stage scrubbers were accumulated in separate storage tanks during each test. Subsequently, they were processed through a sand filter and activated charcoal columns before being discharged into the facility's septic tank system. The hexylene glycol from the second stage scrubber was recirculated during the test periods. A picture of the scrubber system is shown in Figure 4.

Protective Equipment

The experimental facility required two operating personnel when testing liquid pesticide formulations, and four when incinerating solid formulations. All personnel involved with the operation of the facility were provided with hard hats, disposable gloves, safety shoes, work clothes, and disposable coveralls.

During the experimental phase of the facility's operation, i.e., whenever a pesticide was being incinerated, all personnel were supplied with bottled breathing air through demand-flow respirators.

SAMPLING AND ANALYSIS

The major emphasis was given to characterization and quantification of the pesticide (and closely related chemical species) not destroyed by the incineration process so that the efficiency of incineration could be evaluated. To this end, nine sample points were established in the experimental apparatus. These sample points (as well as manometer and thermocouple locations) are shown in Figure 5.

Efficiency of incineration, which was evaluated about the incinerator, was based on analysis of samples from three points (Sample Points Nos. ① , the incinerator feed; ② , the incinerator off-gas; and ③, any solid residues left in the incinerator chambers).

The incinerator off-gas (Sample Point No. ②) was also characterized according to more conventioanl discharge measurements, including SO_2, NO_x, moisture, Orsat analysis for excess air determination, total hydrocarbons, and certain additional special analyses. The additional tests included cyanide analysis (as CN^-) for all nitrogen-containing pesticides (picloram, atrazine, captan, and zineb), and total pyrophosphate analysis of the phosphorus-based pesticide (malathion).

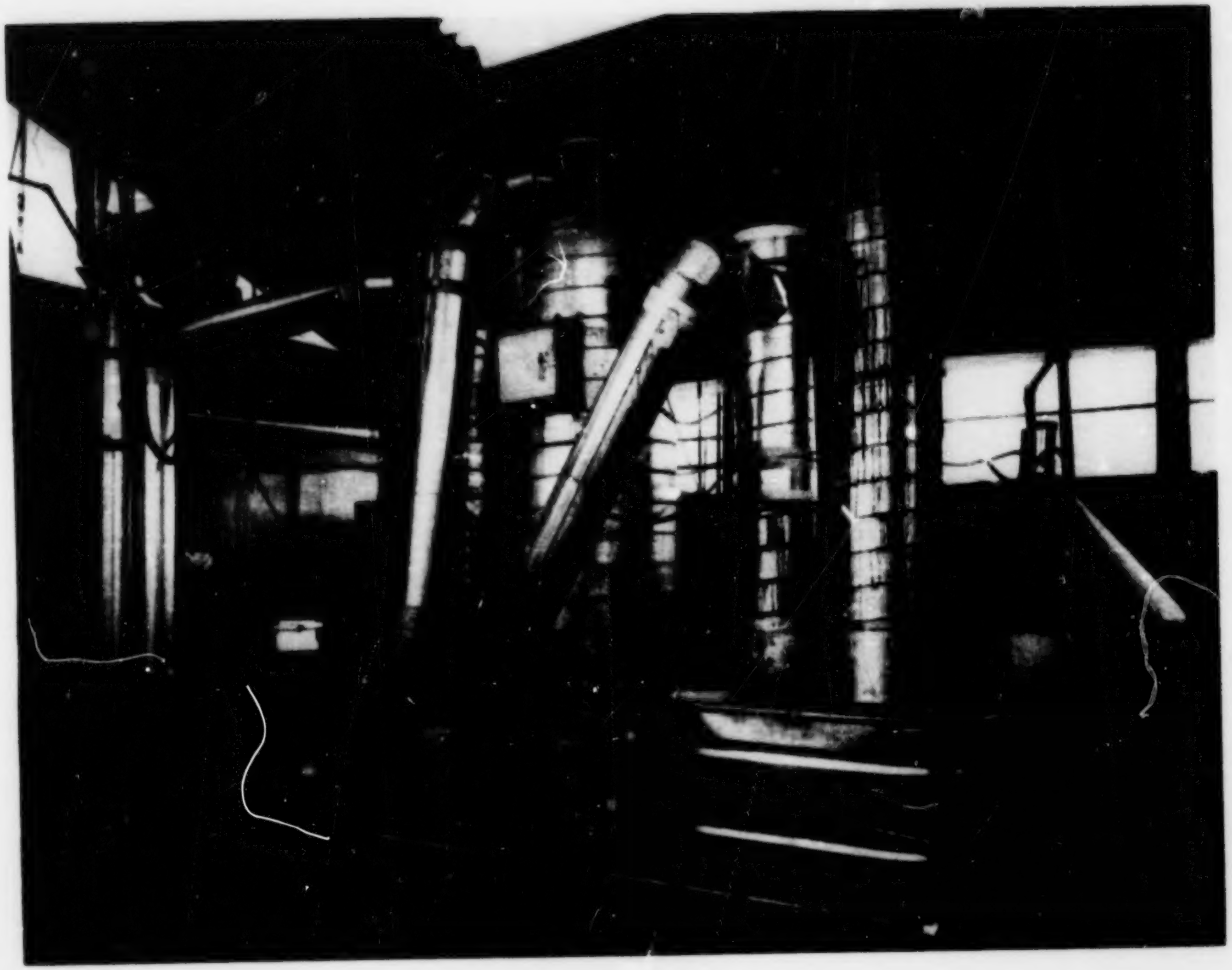


Figure 4. Scrubber system

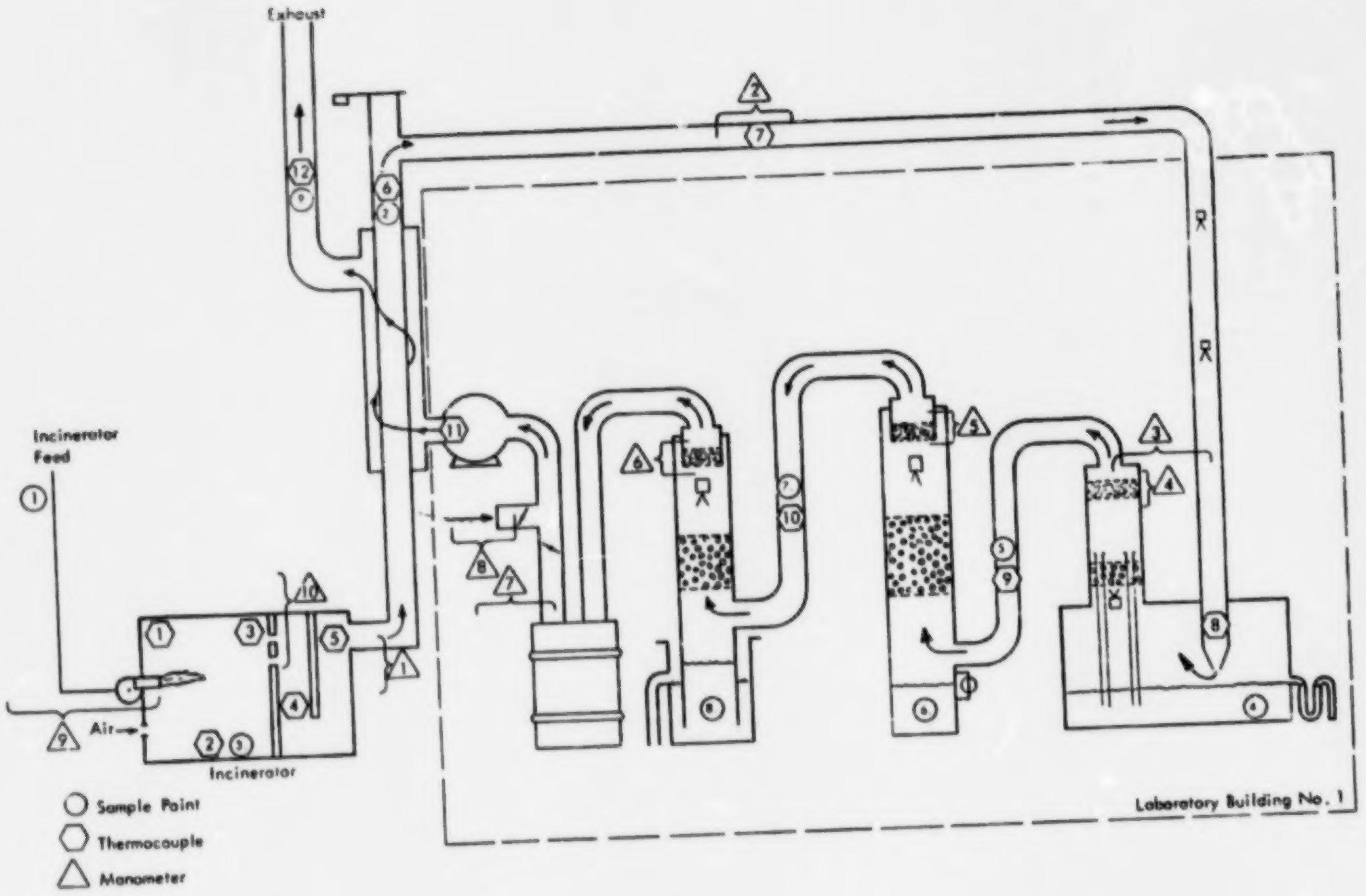


Figure 5. Sample point, thermocouple, and manometer locations

The following two subsections briefly describe the sampling and methods of analysis used during the study. A detailed discussion of the sampling procedures and methods of analysis (excluding methods for active ingredient analysis) is given in Appendix C. The methods of active ingredient analysis are reviewed in detail in the appropriate subsection of Appendix B - Test Results.

Sampling Methods

For liquid pesticide formulations, the method used to obtain gas samples for active ingredient analysis utilized sampling "trains" consisting of mini-impingers, an 0.8 μ filter, a liquid nitrogen cold trap (at Sample Point No. ② (Figure 5) only), and a critical orifice attached to a vacuum system. The first two impingers were filled with 20 ml of the appropriate pesticide grade solvent, while the last impinger was left empty in order to trap any significant carry-over and prevent wetting of the filter element. A 26G x 0.95 cm (3/8-in.) hypodermic needle was used as the critical orifice in each of the four gas sampling trains (Sample Points Nos. ②, ⑤ , ⑦ , and ⑨) used for all liquid formulation experiments to continuously sample the gas stream during a steady state period of about 30 min. The train used for the undiluted incinerator off-gas (Sample Point No. ②) is shown in Figure 6.

For solid pesticide formulations, the potential for losing pesticide-containing dust from the stack made it necessary to determine the stack particulate loading. Sampling the incinerator effluent using only the vapor sampling technique as outlined above for liquid formulation would not reflect the pesticide content of dust emitted.

It was decided that the most accurate evaluation would be obtained by utilizing Method 5 as published in the *Federal Register*[20/] to determine the particulate loading in the stack. This technique, specified by EPA for use in such determinations, gives the total particulate discharged from the incinerator stack. The particulate samples, after collection, were then analyzed for residual pesticides.

Two modifications were made to facilitate the analysis of the sample for pesticide content. First, the appropriate solvent was used in the impingers rather than water. The second modification was to add a liquid nitrogen cold trap to the sample train in order to collect condensibles for active ingredient analysis. After particulate analysis had been completed, all samples were analyzed for active ingredient and related chemical species content.

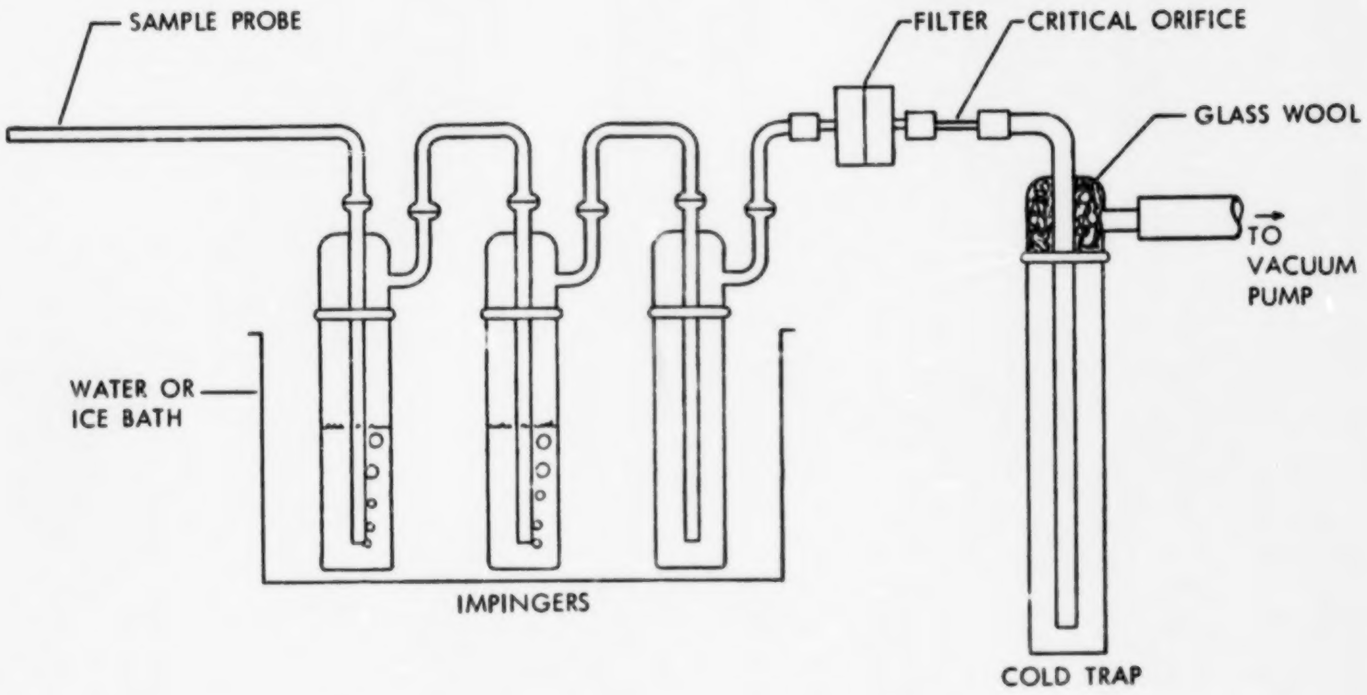


Figure 6. Gas sampling train

Sampling methods for SO_2, NO_x, moisture, and Orsat analysis followed those specified in the Federal Register.[20/] Detailed descriptions of these methods, as well as those used for obtaining representative samples of solid residues and scrubber liquids are described in Appendix C.

Methods of Analysis

Samples from the nine sampling points were analyzed for active ingredient content, and for all other chemically similar, partially degraded species. Active ingredient and total species analyses were performed using the specific method of analysis for each of the pesticides tested. (Details of each method have been included in the appropriate subsection of Appendix B - Test Results.)

Method of analysis used for SO_2, NO_x, moisture, and Orsat determination were those specified in the Federal Register[20/] for such determinations. These methods, as well as those for total hydrocarbons, cyanide (as CN^-), and total pyrophosphate content are detailed in Appendix C.

EXPERIMENTAL DESIGN

DDT, the first pesticide tested, was the only one investigated using the initial concept of statistically designed experiments in order to define optimum incinerator operating conditions. Pesticide injection rate, excess air rate, operating temperature, and turbulence were selected as the operating conditions to be independently varied during experiments using a 43% DDT emulsifiable concentrate (EC) formulation. Retention time and supplemental fuel rate, therefore, were dependent (concomitant) variables. A modified fractional experiment was designed using 16 combinations (high and low levels) of the four independently varied conditions. This initial experiment was then followed with a limited number of tests using a solid (dust) formulation in order to evaluate the effect of physical form on the efficiency with which DDT could be incinerated.

The eight pesticides tested after DDT were evaluated using a two-step approach. First, preliminary laboratory thermal analyses (differential thermal analysis (DTA), and thermal gravimetric analysis (TGA)) were conducted to identify temperatures at which the respective pesticide could be expected to decompose. Following this definition, tests were made in the favorable temperature range utilizing a liquid and a solid formulation. For pesticides commercially available in only solid forms, a minimum of eight tests were conducted using a major solid formulation. The rate of pesticide injection, percent excess air, and operating temperature were varied between two nominal values, i.e., a high and low level.

Test Cycle

The following test cycles were used for all liquid and solid pesticide formulation experiments conducted during the study.

Liquid Formulations Test - The incinerator was preheated prior to the test for approximately 6 hr. During the first 3 to 4 hr, an 11.3 or 13.2 liters/hr (3.0 or 3.5 gal/hr) nozzle was used, depending on: (a) the desired test temperature; and (b) the temperature of the incinerator prior to firing. For the last 2 to 3 hr, the incinerator was preheated with the nozzle that was to be used for the test in order to (a) stabilize the incinerator temperatures; and (b) determine the approximate nozzle feed rate.

During the incinerator warm-up, further preparation was made for the test. Sampling trains were made ready and installed, i.e., pesticide sampling trains, moisture, SO_2, NO_x, CN^- and total pyrophosphate as appropriate to the specific test. The Orsat analyzer, the total hydrocarbons analyzer, and the manometers were standardized. The pesticide formulation was then mixed and weighed.

Approximately 15 min prior to starting pesticide injection, the scrubber system was started by turning on the blower, starting scrubber water and hexylene glycol circulation, and closing the stack bypass (see Figure 1, p. 21). After starting the system, the draft and burner fan openings were adjusted for the anticipated percent excess air. Flow rate tests were run on the sampling trains with a rotometer and Orsat analysis was run on the stack gas. Scrubbers 1 and 3 tanks were pumped outside, and Scrubbers 1, 2, and 3 were measured and sampled just prior to initiating pesticide injection.

After pesticide injection was started, the system was run 15 min before starting the sample trains in order to stabilize the system. An initial sample was taken of the pesticide-fuel oil mixture.

During the sampling time (30 min) the following procedure was followed. Readings were taken each 5 min on temperatures, manometers, fuel oil and pesticide levels, SO_2, and pesticide sampling trains. Three Orsat samples were taken, the exhaust plume was observed as appropriate, and the second sample of the pesticide feed was taken.

Immediately after the 30 min sampling period, pyrometer readings were taken and the second NO_x and incinerator feed samples were collected.

The burner feed was then switched from the pesticide containing mixture to fuel oil and allowed to run for an additional 5 min. During this time, the pesticide feed line was cleaned out, flow rates were again checked on the sampling trains, and the SO_2 train was purged.

The stack bypass was then opened and the blower turned off. The burner continued to operate another 10 to 30 min on fuel oil.

Immediately after the experimental test, Scrubbers 1 and 3 were drained, the fuel oil line was allowed to run dry, the burner was removed from the incinerator, and the sample trains were recovered. Orsat samples were then analyzed, the pesticide drum was reweighed, the tanks of Scrubbers 1, 2, and 3 were measured and sampled, the tanks of Scrubbers 1 and 3 were pumped out, and the stack bypass was closed.

Solid Formulations Test - Prior to beginning the incinerator warm-up, residues from the prior run were cleaned out of the primary and secondary chambers. The residues were weighed, sampled, and the excess residue labeled and stored.

The incinerator was fired approximately 6 hr prior to the test. During the first 3 to 4 hr, the incinerator was operated with a 11.3 or 13.2 liters/hr (3.0 or 3.5 gal/hr) nozzle, depending on the anticipated test temperatures and the temperature of the incinerator prior to firing. During the last 2 to 3 hr, the warm-up was conducted with the intended test nozzle.

During the incinerator warm-up, further preparation was made for the test. Sampling trains were made ready and installed, i.e., pesticide sampling train(s), moisture, SO_2, NO_x, and CN^- or pyrophosphate, as appropriate. The Orsat analyzer, the total hydrocarbons analyzer, and the manometers were standardized. The pesticide formulation was then weighed out, and the feed rate was set and checked.

Prior to starting the pesticide injection, the scrubber system was started for approximately 15 min by turning on the blower, starting the scrubber water and hexylene glycol circulation, and closing the stack bypass. After starting the system, the draft and burner fan openings were adjusted for the anticipated percent excess air, and flow rate tests were run on the sampling trains. Orsat analysis was run on the stack gas, and the particulate sampling train (Sample Point No. ②) was leak checked.

After the pesticide injection was started, the system was run 15 to 30 min before starting the sample trains. During this time, final adjustments of the draft were made, an Orsat analysis was run, and an NO_x sample was taken. Scrubbers 1 and 3 tanks were pumped outside just prior to starting the sampling. A sample of the pesticide formulation was taken.

During the sampling period (60 min), a number of measurements were made. Scrubbers 1, 2, and 3 tanks were measured and sampled immediately after the start of sampling, as appropriate. Readings were taken each 5 min on temperatures, manometers, fuel oil level, SO_2 and pesticide sampling train(s). During the test, four Orsat samples were taken, and the exhaust plume was observed. Pyrometer readings were taken midway of the sampling period (after 30 min).

After the 60 min sampling period, another NO_x sample was taken and the system was allowed to run 5 to 10 min on fuel oil during which time the second pesticide sample was taken, the excess pesticide was cleaned out of the vibrating screw feeder and weighed, flow rates were again run on the sampling trains, the SO_2 train was purged, and Scrubbers 1 and 3 tanks were measured and sampled.

The stack bypass was then opened and the blower turned off. The burner continued another 10 to 30 min.

After the experimental test, the burner was removed from the incinerator, sample trains were recovered, and the Orsat samples were analyzed. Scrubbers 1 and 3 tanks were pumped out.

SECTION V

RESULTS

This section summarizes the major findings from the pilot-scale incineration of DDT, aldrin, picloram, malathion, toxaphene, atrazine, captan, zineb, and mirex. The measure of performance that has been used to evaluate test results is the extent (efficiency) to which the pesticidally active chemical species (active ingredient) was decomposed within the incinerator during a period of steady state operation. This efficiency, expressed as a percentage, equals $\left[1 - \frac{\text{Quantity \underline{out}}}{\text{Quantity \underline{in}}}\right] \times 100$. The Quantity in (the amount of active ingredient fed into the incinerator) has been determined by volumetric measurement and quantitative analysis of the pesticide-containing mixture injected into the incinerator (Sample Point No. ① , Figure 5, page 27). Representative samples of the undiluted incinerator off-gas (Sample Point No. ②) were analyzed, and in combination with a determination of the total volume of undiluted gas, were used to determine the amount of pesticide in the effluent gas. Analogous determinations were made for any solid residue (Sample Point No. ③) left in the incinerator, e.g., from tests involving dust, wettable powder, pellet, bait, or granular formulations. The amount of pesticide remaining in the incinerator off-gas and residues was defined as the Quantity out.

Whenever possible, a second efficiency was calculated using the same equation, but where the Quantity out included not only the unburned pesticide as such, but also all other closely related, partially decomposed chemical species detected; this quantity has been termed total species. Thus, for DDT as an example, the Quantity out (total species) included DDT plus all other chlorinated hydrocarbon species detected in the incinerator off-gas and any solid residues.

Other constituents of the incinerator off-gas, i.e., SO_2, NO_x, CO, CO_2, total hydrocarbons, CH_4, and (where applicable) CN^-, were not included in the efficiency calculations.

Preceding page blank

The results from the incineration tests are presented in four following subsections: Specific Results, General Findings, System Performance, and Problem Areas.

The specific results subsection briefly summarizes the major test results for each of the nine pesticides in the chronological order of their investigation. Complete details of the test conditions and results are given in Appendix B.

The general findings subsection reviews the overall efficiencies of incineration for the subject pesticides as well as general problem areas that were encountered.

The last two subsections (Systems Performance and Problem Areas) address the adequacy of the experimental apparatus used for the tests as well as problems associated in its operation.

SPECIFIC RESULTS

DDT

DDT was specified by the EPA project officers as the first pesticide to be studied because it not only represents existing disposal problems but also has been the subject of other research studies. The DDT experiments, therefore, provided data on its combustion as well as a means for relating our findings to those from other research.

There are a number of operating conditions that can influence the performance of an incinerator used for pesticide disposal. These include pesticide injection rate, operating temperature, excess air rate, turbulence, auxiliary fuel rate, and retention time. The interaction of many of these factors, however, is such that they cannot all be independently varied. Pesticide injection rate, excess air rate, operating temperature, and turbulence were selected as the operating conditions to be independently varied during the DDT experiments. Retention time and supplemental fuel rate were dependent (concomitant) variables.

A modified fractional factorial experiment was designed to study the combustion of a 25% DDT emulsifiable concentrate (EC) formulation in order to determine optimum incineration conditions. The four controlled variables (each at two levels) were to be run in 16 combinations.

The 25% EC formulation was initially injected at a nominal rate of 3.4 kg (7.5 lb) DDT* per hour, while the second level of injection was one-half of the initial rate. A standard fuel oil burner was used as the injection system (see the subsection of Experimental Facilities, page 20 for a more detailed description of the feed system).

Air was injected at approximately 50 and 150% excess (calculated according to Method 3 of "Standards of Performance for New Stationary Sources,")[20] and the incinerator temperature was varied from approximately 950°C (1750°F) to 1090°C (2000°F), the nominal operating range of the experimental incinerator with the available fuel oil burner. The temperature was obtained by injecting the desired amounts of DDT (in the EC formulation) mixed with the appropriate amount of supplemental fuel (No. 2 fuel oil).

Turbulence within the ignition chamber was influenced by changing the location of the pesticide injector. The two levels of turbulence were studied by injecting the EC-fuel oil mixture through the fuel oil burner in the front (primary) and in the side (alternate) position of the primary combustion chamber (see Figure 2, page 22).

Thus, the fractional factorial experiment was as shown on the following page.

A total of 21 tests were conducted to fit the 16 points of a modified fractional factorial analysis of these four parameters.

The results of the 21 tests made using the 25% EC formulation are summarized in Table 3. For all but four tests, the efficiency of incineration was > 99.99%, based on either DDT or total species detected. The operational data show that we were not able to operate the incinerator precisely at the desired levels for each independent variable, e.g., 50 and 150% excess air. For this reason, the data could not be strictly evaluated as representing a fractional factorial experiment. Therefore, the data were evaluated using multiple regression analysis, which is the more appropriate statistical technique in this instance because of the uniformly high combustion efficiencies observed. Regressions of the four

---

* For purposes of this report, "DDT" has been defined to include four major isomers commonly found in the technical material, i.e., p,p'-DDT, o,p'-DDT, p,p'-DDE, and o,p'-DDE. Both o,p'-DDD and p,p'-DDD have been arbitrarily included with the "other" chlorinated hydrocarbon species.

Experiment designation	Turbulence	Pesticide injection rate	Operating temperature	Excess air rate
A	a	c	e	g
B	a	c	e	h
C	a	c	f	g
D	a	c	f	h
E	a	d	e	g
F	a	d	e	h
G	a	d	f	g
H	a	d	f	h
I	b	c	e	g
J	b	c	e	h
K	b	c	f	g
L	b	c	f	h
M	b	d	e	g
N	b	d	e	h
O	b	d	f	g
P	b	d	f	h

---

a = frontal injection
b = side injection
c = 1.70 kg (3.75 lb) DDT per hour
d = 3.4 kg (7.5 lb) DDT per hour
e = 950°C (1750°F)
f = 1090°C (2000°F)
g = 50%
h = 150%

Table 3. SUMMARY OF TEST RESULTS--25% DDT EC FORMULATIONS

Experiment designation	DDT rate g/hr (lb/hr)	Turbulence [a]	Primary chamber temperature °C (°F)	Excess air %	Retention time sec Primary chamber	Retention time sec Second chamber	Ratio of DDT in off-gas to DDT fed	Ratio of total species content of off-gas to DDT fed	Incinerator efficiency % DDT	Incinerator efficiency % Total species
A	1,090 (2.42)	1	1040 (1900)	92	2.5	2.7	5×10^{-6}	2.9×10^{-5}	> 99.99	> 99.99
B	1,910 (4.23)	1	940 (1730)	162	1.3	1.2	1.8×10^{-5}	2.7×10^{-5}	> 99.99	> 99.99
C	1,950 (4.27)	1	1140 (2090)	88	1.6	1.8	4.9×10^{-6}	1.2×10^{-5}	> 99.99	> 99.99
	1,770 (3.88)	1	1170 (2130)	100	1.5	1.6	9×10^{-6}	2.1×10^{-5}	> 99.99	> 99.99
D	1,630 (3.59)	1	1040 (1900)	120	0.9	0.7	1.1×10^{-4}	1.7×10^{-4}	> 99.98	> 99.98
E	1,320 (2.90)	1	1050 (1930)	85	2.4	2.4	5×10^{-6}	3.0×10^{-5}	> 99.99	> 99.99
F	4,630 (10.25)	1	930 (1700)	143	1.0	0.8	5×10^{-5}	5×10^{-5}	> 99.99	> 99.99
G	2,400 (5.29)	1	1150 (2110)	116	2.2	2.3	2.8×10^{-5}	7×10^{-5}	> 99.99	> 99.99
H	2,400 (5.34)	1	1050 (1920)	135	0.9	0.7	4×10^{-5}	5×10^{-5}	> 99.99	> 99.99
I	1,450 (3.16)	2	1070 (1950)	83	2.9	3.0	2.8×10^{-5}	6×10^{-5}	> 99.99	> 99.99
J	1,220 (2.74)	2	980 (1800)	138	3.1	3.2	6×10^{-5}	1.4×10^{-4}	> 99.99	> 99.98
	1,130 (2.53)	2	980 (1800)	128	2.5	2.9	1.2×10^{-5}	2.3×10^{-5}	> 99.99	> 99.99
K	1,450 (3.21)	2	1170 (2140)	64	1.4	1.4	3.5×10^{-5}	9×10^{-5}	> 99.99	> 99.99
L	1,500 (3.34)	2	1050 (1930)	151	1.4	1.3	3.8×10^{-5}	1.2×10^{-4}	> 99.99	> 99.98
	500 (1.09)	2	1100 (2010)	137	1.6	1.4	5×10^{-5}	6×10^{-5}	> 99.99	> 99.99
	730 (1.62)	2	1090 (2000)	163	1.3	1.3	5×10^{-5}	6×10^{-5}	> 99.99	> 99.99
M	1,860 (4.11)	2	1030 (1890)	96	1.5	1.6	3.4×10^{-5}	9×10^{-5}	> 99.99	> 99.99
N	1,810 (3.96)	2	940 (1730)	166	3.0	3.1	4.4×10^{-5}	1.6×10^{-4}	> 99.99	> 99.98
O	3,220 (7.08)	2	1190 (2180)	80	1.7	1.6	7×10^{-6}	1.8×10^{-5}	> 99.99	> 99.99
P	3,360 (7.36)	2	1030 (1890)	164	1.3	1.2	2.4×10^{-5}	2.6×10^{-5}	> 99.99	> 99.99
	1,810 (4.03)	2	1050 (1930)	130	1.5	1.3	3.0×10^{-5}	4.9×10^{-5}	> 99.99	> 99.99

---

[a] 1 = Frontal injection
2 = Side injection

quantitative variables (DDT injection rate, retention time, temperature, and excess air) were run using: (a) the relative amount of DDT not destroyed ("Ratio of DDT in Off-Gas to DDT Fed" column of Table 3); and (b) the relative amount of total chlorinated hydrocarbon species not destroyed ("Ratio of Total Species Content of Off-Gas to DDT Fed" column of Table 3) as the dependent variable (y_i).

A multiple regression model, $y_i = \alpha_0 + \alpha_1 X_{1i} + \alpha_2 X_{2i} + \alpha_3 X_{3i} + \alpha_4 X_{4i} + C_i$, was used to perform an analysis of variance (ANOVA) in order to furnish values (F-values) which could be used to decide whether or not predicting y_i (relative efficiencies of combustion, based on either the DDT or total chlorinated species left undestroyed) by using the model results in significantly more accurate results than "predicting" y_i by random choices from the y_i distribution.

In neither case was the regression found to be significant, nor were any of the individual regression coefficients found to be significant. Thus, knowledge of the DDT feed rate, primary chamber temperature, excess air, and retention time, over the ranges investigated did not materially aid in predicting the incineration efficiency.

The DDT efficiencies determined from these experiments are not unlike those reported in an earlier study by the Defence Research Establishment of Canada. Their report showed that no more than 0.0002% of the DDT entering their incinerator remained unburned.[21] Our results, reported to the same number of decimal points, indicate 0.0005% DDT remained unburned (Experiments A and C, Table 3).

Upon completion of experiments with the 25% DDT EC formulation, eight tests were made using a 10% dust formulation. These limited additional tests were made in order to evaluate the effect of physical form on the previously established efficiency of DDT combustion.

Turbulence was varied for the dust experiments by injecting the dust horizontally from two positions. For Configuration 1, both the dust injection nozzle and the fuel oil burner were located in the front burner position (see Figure 2, page 22). The dust was injected horizontally at a 30-degree angle to the fuel oil burner, as shown in Figure 3, page 24. For Configuration 2, the oil burner was located in the front (primary) position, while the dust injection nozzle was located in the side (alternate) position. Thus, the centerlines of the burner flame and dust stream in Configuration 2 impinged at 90 degrees on a horizontal plane at the geometric center of the primary chamber.

Data from the eight 10% DDT dust experiments are summarized in Table 4. The incineration efficiency figures reported in the last two columns of the table are based on (a) the total unburned DDT and (b) total species found in the effluent gas and the solid residue deposited on the walls and in the bottom of the incinerator. Thus, the Quantity out values used to calculate the two efficiencies include the amount of material in the gas evolved during the 60-min sampling period, plus the appropriate fraction of the content of the total solid residue recovered from the incinerator. These efficiencies are comparable to those obtained from the incineration of the 25% DDT EC formulation. Thus, the physical form of the DDT formulation had no significant effect on the efficiency with which DDT was incinerated.

Method 5 of "Standards of Performance for New Stationary Sources,"[20/] was used to determine the particulate loading in the stack. This technique, specified by EPA for use in such determinations, gave the total dust particulate discharged from the incinerator stack. The particulate samples, after collection, were then analyzed for residual DDT and total species content.

Two modifications of the standard particulate sampling train were made to facilitate the analysis of the sample for DDT content. First, pesticide grade benzene was used in the impingers rather than water. (The substitution of an appropriate solvent was made for all of the pesticides tested.) The second modification was to add a liquid nitrogen cold trap to the sample train in order to collect condensibles for DDT and total chlorinated hydrocarbon analysis. After particulate analysis had been completed, all samples were analyzed for DDT content.

The results of the particulate loading analyses for the 10% DDT dust adjusted to 12% CO_2, are also given in Table 4. The value for particulate loading, according to Title 40, CFR (Part 60, Subpart 60.50), must not exceed 183 mg/m^3 (0.08 gr/dscf) on any new facility with a capacity $\geq 4.5 \times 10^4$ kg/day (50 tons/day). This indicates that an incinerator, if required to meet these federal regulations while incinerating the 10% DDT dust formulation, would require emission control.

Significant corrosion was noted during the system cleanup after completion of the DDT experiments, primarily in the first water scrubber (see Figure 1, page 21). Both the concial reducer nozzle and the demister pad (constructed of 304 stainless steel) had been almost entirely corroded out. Corrosion was also noted on the tank section of the first scrubber, on the vertical piping leading down to the first water scrubber, and on two water nozzles in that section of pipe.

Table 4. SUMMARY OF TEST RESULTS--10% DDT DUST FORMULATIONS

Experiment designation	DDT rate g/hr (lb/hr)	Turbulence	Primary chamber temperature °C (°F)	Excess air %	Retention time sec		Particulate loading mg/m³ (gr/dscf)	Ratio of DDT in off-gas to total DDT fed	Ratio of total species in off-gas to total DDT fed	Incinerator efficiency %	
					Primary chamber	Second chamber				DDT	Total species
A	1010 (2.22)	2	1210 (2210)	79	1.4	1.4	23,700 (10.3)	1.7×10^{-5}	2.3×10^{-5}	> 99.99	> 99.99
B	930 (2.10)	1	1140 (2080)	58	1.9	2.0	23,400 (10.2)	6×10^{-5}	1.0×10^{-4}	> 99.99	> 99.98
C	980 (2.16)	1	930 (1710)	164	1.4	1.2	29,000 (12.6)	9×10^{-6}	1.7×10^{-5}	> 99.99	> 99.99
D	1020 (2.24)	1	1030 (1880)	84	2.4	2.5	51,000 (22.1)	7×10^{-6}	1.0×10^{-5}	> 99.99	> 99.99
E	1720 (3.80)	1	1010 (1850)	128	1.3	1.2	41,000 (17.8)	9×10^{-6}	1.0×10^{-5}	> 99.99	> 99.99
F	2230 (4.91)	1	1120 (2050)	111	2.0	2.0	63,000 (27.3)	9×10^{-6}	1.2×10^{-5}	> 99.99	> 99.99
G	2230 (4.91)	1	1020 (1860)	156	1.6	1.6	71,000 (30.8)	7×10^{-6}	9×10^{-6}	> 99.99	> 99.99
H	1010 (2.22)	2	1030 (1880)	126	2.1	2.2	35,000 (34.0)	1.2×10^{-5}	1.7×10^{-5}	> 99.99	> 99.99

Aldrin

The experimentation with aldrin (and the seven additional pesticides subsequently studied) involved two phases. First, differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were made to identify potentially favorable combustion temperatures for each pesticide. Experiments were then conducted in the pilot-scale incinerator to verify the efficiency of combustion in the range of potentially favorable operating temperatures. A minimum of eight experiments utilizing a liquid formulation and four utilizing the solid formulation were made. For pesticides commercially available in only solid forms, a minimum of eight tests were conducted using a major solid formulation. Rate of pesticide incineration, percent excess air, and operating temperature were varied between two nominal values, i.e., a "high" and "low" level.

DTA of a sample of recrystallized aldrin obtained by evaporation of a sample of the EC formulation showed two endotherms, one at 60 to 66°C, and the other at 210 to 250°C. The first endotherm indicates a phase change (TGA data showed no significant weight loss at 60 to 70°C). The latter endotherm could very well be the vaporization of the liquid. Significant weight loss was observed at this temperature from the TGA data. Beyond 250°C, however, an exothermic process was observed which indicated that the sample was undergoing decomposition. This was substantiated by TGA which showed continued weight loss all the way to about 570°C. At this temperature, virtually no sample remained.

DTA analyses of the 19% granular formulation of aldrin data showed two decomposition processes--one at ~ 175°C and the other at ~ 370°C. This was substantiated by the TGA which showed continuous weight loss as temperature increased. At about 270°C almost 25% of the original weight was gone, which exceeds the ~ 19% aldrin content of the formulation. As the heating of the formulation continued to 700°C, another 10% was lost. From 700° to 1000°C, essentially no weight loss was recorded. These data indicate that the aldrin in this formulation would be destroyed at 700°C.

Initially, eight tests were made using the EC formulation of aldrin. The results of these tests (as well as two subsequent tests) are given in Table 5. Efficiencies of combustion was again defined in terms of the incinerator, i.e., aldrin charged into the system (Quantity in) versus aldrin (and total chlorinated species) not destroyed in the incinerator (Quantity out). The efficiencies for the eight initial tests were all > 99.99%, based on either aldrin, or total chlorinated hydrocarbon species detected. However, all of the initial eight tests were made at temperatures significantly above those indicated (by DTA and TGA) as being potentially favorable for aldrin degradation. This was due to the operating limit of the available fuel oil burner, which was designed to burn from 11.3 to 30.3 liter/hr (3.0 to 8.0 gal/hr) of No. 2 fuel oil.

Table 5. SUMMARY OF TEST RESULTS--41.2% ALDRIN EC FORMULATION

Run No.	Aldrin rate g/hr (lb/hr)	Primary chamber temperature °C (°F)	Excess air %	Retention time sec		Ratio of aldrin content of off-gas to aldrin fed	Ratio of total species content of off-gas to aldrin fed	Incineration efficiency %	
				Primary chamber	Second chamber			Aldrin	Total species
1	2,310 (5.09)	940 (1730)	209	2.5	2.3	1.2×10^{-7}	6×10^{-6}	> 99.99	> 99.99
2	3,480 (7.67)	1020 (1870)	128	1.9	1.6	1.5×10^{-7}	9×10^{-6}	> 99.99	> 99.99
3	2,470 (5.44)	1020 (1870)	144	2.0	1.9	2.4×10^{-7}	4.4×10^{-6}	> 99.99	> 99.99
4	1,610 (3.56)	920 (1690)	230	4.8	5.1	2×10^{-7}	3×10^{-6}	> 99.99	> 99.99
5	1,650 (3.63)	830 (1530)	203	4.3	4.6	2×10^{-7}	5×10^{-6}	> 99.99	> 99.99
6	660 (1.45)	850 (1560)	158	4.2	4.5	3×10^{-7}	3×10^{-6}	> 99.99	> 99.99
7	2,260 (4.98)	1050 (1920)	149	1.2	1.2	1.1×10^{-7}	3×10^{-6}	> 99.99	> 99.99
8	1,350 (2.98)	1140 (2080)	70	2.2	2.2	1.7×10^{-7}	2.6×10^{-6}	> 99.99	> 99.99
9	1,010 (2.23)	680 (1250)	332	4.8	5.3	1×10^{-6}	3×10^{-5}	> 99.99	> 99.99
10	620 (1.36)	600 (1120)	380	6.9	7.6	6×10^{-7}	2×10^{-5}	> 99.99	> 99.99

Subsequently, two additional tests (Nos. 9 and 10) were made using a new fuel oil burner capable of operating at lower feed rates than the burner previously used; the lower rates were used to conduct the two additional runs at much lower temperatures. Runs Nos. 9 and 10, although conducted at primary chamber temperatures 400 to 500°C (800 to 900°F) lower than the initial eight runs, also showed an efficiency of aldrin incineration of > 99.99%, based on aldrin or the total chlorinated species detected. The relative amounts of chlorinated species generated during Runs Nos. 9 and 10 (as shown by the "Ratio of Total Species Content of Off-Gas to Aldrin Fed" column in Table 5), however, were significantly higher than that for the tests conducted at higher temperatures. The relative aldrin content of the off-gas was also somewhat higher for the last two tests (see Table 5). Thus, incineration of aldrin at ~ 650°C (1200°F) is virtually as efficient as incineration at ~ 1090°C (2000°F) in terms of actual aldrin content, but is less efficient in terms of chlorinated hydrocarbons in the incinerator effluent.

A granular formulation of aldrin was used to evaluate the effect of physical form on the efficiency of aldrin incineration. The results of these tests, which are summarized in Table 6, also showed an efficiency of > 99.99% in all cases.

The particulate emission rates, corrected to 12% CO_2, were above the standard of 183 mg/m^3. Incineration of the aldrin granular formulation, if required to meet federal regulations, would require emission control.

Upon completion of the aldrin experiments, the interior surfaces of the incinerator and duct work were inspected for deposits. Samples were taken of a thin layer of residue that had deposited on the walls of the stack from the incinerator and in the horizontal run of duct leading to the scrubber system. Neither aldrin nor any of the major components of technical grade DDT (p,p'-DDT, o,p'-DDT, p,p'-DDE, o,p'-DDE, p,p'-DDD, and o,p'-DDD) were detected in these samples.

No problems were encountered with the incineration of aldrin. The solid residue left in the primary chamber of the incinerator when incinerating the granular formulation at the higher temperatures, however, became very hard and compacted. In fact, these residues had to be chipped out of the incinerator and ground before being analyzed.

Picloram

DTA of picloram (4-amino-3,5,6-trichloropicolinic acid as the potassium salt) pellets showed one endotherm at about 90°C. Beyond 90°C, the sample showed a continuous decomposition process all the way to the

Table 6. SUMMARY OF TEST RESULTS--19% ALDRIN GRANULAR FORMULATION

Run No.	Aldrin feed rate g/hr (lb/hr)	Primary chamber temperature °C (°F)	Excess air %	Retention time sec		Particulate loading mg/m^3 (gr/dscf)	Ratio of aldrin in off-gas to total aldrin fed	Ratio of total species in off-gas to total aldrin fed	Incineration efficiency %	
				Primary chamber	Second chamber				Aldrin	Total species
A	1,860 (4.09)	1150 (2100)	48	2.5	2.7	1,830 (0.79)	2.1×10^{-7}	1.8×10^{-6}	> 99.99	> 99.99
B	1,690 (3.73)	980 (1800)	155	2.2	2.6	1,420 (0.62)	1.6×10^{-5}	2.0×10^{-5}	> 99.99	> 99.99
C	3,630 (8.01)	890 (1630)	81	3.2	3.6	2,430 (1.06)	2.3×10^{-7}	1.4×10^{-6}	> 99.99	> 99.99
D	3,740 (8.24)	1030 (1890)	120	2.0	2.2	1,560 (0.68)	7×10^{-8}	1.0×10^{-6}	> 99.99	> 99.99
E	3,630 (8.00)	1100 (2020)	118	1.4	1.4	1,970 (0.85)	3.3×10^{-7}	9×10^{-7}	> 99.99	> 99.99
F	1,830 (4.03)	860 (1580)	113	3.0	3.2	1,380 (0.60)	1.9×10^{-8}	8×10^{-7}	> 99.99	> 99.99

instrument operational limit (400°C). This decomposition process was supported by the weight loss shown by TGA. The total weight loss up to 400°C was approximately 12% compared to the nominal 11.6% picloram salt content of the pellets.

DTA of a sample of recrystallized picloram obtained by the evaporation of the 21.5% potassium salt formulation showed endotherms at 68 to 80°C, and 144 to 154°C. Once past the second endotherm, decomposition started and exotherms at 222, 302, and 353°C were observed. The decomposition process continued to the instrument operational limit (400°C). The TGA data showed no significant weight loss at the two endotherm temperature ranges, thus indicating possible phase changes. However, from 180 to 360°C, about 60% weight loss was observed. Weight loss continued from 360 to 500°C and about 800 to 900°C. At 900°C virtually no sample remained. These laboratory data indicated that picloram would be destroyed before 900°C.

Kennedy et al.[13/] also conducted DTA of picloram. Based on their laboratory analyses, Kennedy et al. concluded that the temperatures for complete combustion of a picloram reference standard and 11.6% picloram solution were 550°C (1022°F) and 640°C (1184°F), respectively.

Initially, seven experiments were made using a water based liquid formulation of picloram (24.9% as the potassium salt, 21.5% acid equivalent). Because this formulation was not miscible with No. 2 fuel oil, a modification of the incinerator feed system was required. (All miscible pesticide formulations were mixed in the appropriate ratio with fuel oil and injected through the primary burner position of the incinerator with an oil burner.) Two separate systems were used to inject fuel oil and the picloram formulation into the primary chamber of the incinerator on a horizontal plane. A standard oil burner was used for the fuel oil. The undiluted picloram was pumped into the incinerator through a fuel oil nozzle of the same type being used in the oil burner. These injection systems were positioned so that the picloram and the flame from the fuel oil burner impinged at an angle of 30 degrees and at a point about 9 cm (3 in.) from the front wall of the incinerator. This is the same configuration that is used to inject solid pesticide formulations (see Appendix A for a more detailed description of the pesticide feed systems). The results of the seven initial tests (as well as two subsequent tests) have been summarized in Table 7.

Two efficiencies of combustion have been calculated to evaluate the results of the picloram tests. The first considered only the picloram in the incinerator input and discharge. This efficiency calculation shows that > 99.99% of the picloram injected into the incinerator was at least

Table 7. SUMMARY OF TEST RESULTS--21.5% PICLORAM LIQUID FORMULATION

Run No.	Picloram rate g/hr (lb/hr)	Primary chamber temperature °C (°F)	Excess air %	Retention time sec		Ratio of picloram in off-gas to picloram fed	Ratio of total species in off-gas to total picloram fed	Incineration efficiency %	
				Primary chamber	Second chamber			Picloram	Total species
1	1,870 (4.12)	530 (990)	298	7.6	8.0	2×10^{-6}	2×10^{-3}	> 99.99	> 99.83
2	1,380 (3.05)	600 (1120)	193	6.7	6.9	1×10^{-6}	4×10^{-4}	> 99.99	> 99.95
3	1,510 (3.33)	630 (1160)	187	6.6	6.8	3×10^{-7}	4×10^{-3}	> 99.99	> 99.63
4	1,290 (2.84)	930 (1700)	62	3.9	4.0	2×10^{-6}	2×10^{-4}	> 99.99	> 99.98
5	1,110 (2.45)	1010 (1850)	130	1.4	1.4	2.3×10^{-5}	3.6×10^{-5}	> 99.99	> 99.99
6	3,470 (7.64)	1030 (1880)	116	1.2	1.2	2.0×10^{-6}	1.3×10^{-5}	> 99.99	> 99.99
7	2,230 (4.92)	800 (1470)	77	6.0	5.8	4×10^{-7}	2×10^{-3}	> 99.99	> 99.78
8	3,270 (7.22)	1000 (1840)	114	1.9	1.8	9×10^{-6}	1.1×10^{-5}	> 99.99	> 99.99
9	2,450 (5.40)	1010 (1850)	50	2.6	2.5	3.7×10^{-5}	4.1×10^{-5}	> 99.99	> 99.99

partially degraded at all temperatures tested, 530 to 1030°C (990 to 1880°F). This is not unexpected as picloram has been reported to decompose at about 216°C (420°F).[22]

The second efficiency calculation includes not only the picloram that is left in the incinerator effluent but also the other chemical species trapped in the sample collection system. Using this calculation, only the two tests (of the seven initial tests) conducted at 1010 and 1030°C showed an efficiency of > 99.99%. As will be discussed later, these two tests also showed significantly lower concentrations (and quantities) of cyanide (CN^-) in the incinerator effluent.

In order to evaluate the effect of physical form on the efficiency with which picloram can be incinerated, five tests were made using a pellet formulation (~ 11.6% picloram as the potassium salt, 10% as the acid equivalent). Results from these five experiments (as well as two subsequent additional tests) are summarized in Table 8.

As was done for the experiments using the liquid formulation, two efficiencies of combustion were calculated. The first considers only the quantity of picloram in the incinerator input and discharge. This efficiency calculation shows that > 99.99% of the picloram injected into the incinerator was at least partially degraded during the first five tests, conducted at temperatures of 640 to 1020°C and primary chamber retention times of 6.9 to 1.3 sec.

The second efficiency calculation includes not only the picloram that is left but also other chemical species (volatile chlorinated hydrocarbons). Using this calculation, only the two tests conducted at the higher temperatures (930 and 1020°C) showed an efficiency of > 99.99%. These initial tests, as well as those using the liquid formulation, indicate that temperatures of about 1000°C and primary retention time of about 1.5 sec are required to satisfactorily incinerate picloram.

The results of the particulate sampling conducted on the picloram pellet tests showed that the grain loadings for all tests exceeded what can be considered low emissions and indicate the need for a particulate control device when incinerating picloram pellets.

Subsequently, four additional tests were conducted to better define the temperature required to reduce cyanide concentration in the incinerator effluent gas to < 1 mg/m^3. Two additional tests were made using the liquid formulation (Runs Nos. 8 and 9, Table 7), and two were made using the pellet formulation (Runs Nos. F and G, Table 8).

Table 8. SUMMARY OF TEST RESULTS--10% PICLORAM PELLET FORMULATION

Run No.	Picloram rate g/hr (lb/hr)	Primary chamber temperature °C (°F)	Excess air %	Retention time sec		Particulate loading mg/m^3 (gr/dscf)	Ratio of picloram in off-gas to picloram fed	Ratio of total species in off-gas to total picloram fed	Incineration efficiency %	
				Primary chamber	Second chamber				Picloram	Total species
A	1,270 (2.8)	1020 (1870)	93	1.3	1.4	357 (0.155)	$< 8 \times 10^{-9}$	2.5×10^{-6}	> 99.99	> 99.99
B	1,270 (2.8)	930 (1710)	170	2.1	2.2	1,060 (0.46)	$< 5 \times 10^{-8}$	2.3×10^{-5}	> 99.99	> 99.99
C	1,180 (2.6)	640 (1190)	226	6.9	7.6	2,900 (1.26)	$< 6 \times 10^{-8}$	2×10^{-4}	> 99.99	> 99.96
D	2,360 (5.2)	710 (1310)	227	6.7	7.3	7,800 (3.4)	2×10^{-8}	2×10^{-4}	> 99.99	> 99.93
E	2,360 (5.2)	930 (1700)	72	4.6	4.9	20,100 (8.7)	3×10^{-6}	2×10^{-4}	> 99.99	> 99.97
F	2,350 (5.2)	950 (1750)	73	2.6	2.6	2,750 (1.19)	4.7×10^{-7}	1.9×10^{-6}	> 99.99	> 99.99
G	2,270 (5.0)	920 (1680)	145	1.9	1.7	1,600 (0.69)	6.8×10^{-7}	1.3×10^{-6}	> 99.99	> 99.99

For the liquid formulation tests, only those experiments conducted in the higher temperature ranges, 1000 to 1030°C (1840 to 1880°F), produced low concentrations (and quantities) of cyanide in the off-gas. Low concentrations (< 1 mg/m^3) and quantities of cyanide (as CN$^-$) were generally also produced from the pellet formulation tests conducted at the higher temperature, 930 and 950°C (1710 and 1750°F). These data indicate that a temperature of about 1000°C for 1.5 sec and sufficient excess air (~ 100%) are required to reduce cyanide generation to < 1 mg/m^3.

Additional samples were also taken during the supplemental pellet formulation experiments (Runs Nos. F and G, Table 8), using a special sampler designed to "catch" pellets as they fell through the combustion chamber in order to approximate the degree of decomposition actually occurring during the first few seconds.

These samples showed that > 90% of the picloram (as well as the other chlorinated species) was "removed" from the pellet during the first 2 sec residence time in the primary chamber. The ~ 10% of the picloram left in the pellets after 2 sec demonstrates (a) the need to insure adequate retention of solid residues in the primary combustion chamber and (b) the inadequacy of conventional retention time calculations (based on the volume of gas) in defining solid residue retention.

The incineration of picloram in both the liquid and the pellet formulations can be classified as giving relatively dirty burns. A dark (bluish) exhaust plume was discharged from the experimental system during most of the tests.

The dirtiness of the burns caused minor plugging problems with the demister pad in the first stage water scrubber. This problem was particularly noticeable when operating the incinerator at low draft.

Malathion

DTA and TGA of 25% malathion wettable powder (WP) formulation indicated that a rather slow decomposition of malathion took place. The DTA data showed no prominent exotherms or endotherms; TGA data indicated slow weight loss as temperature increased. At about 650°C, almost 30% of the original weight was gone; essentially no more weight loss was observed from 650 to 1000°C.

DTA of malathion obtained by evaporation of a sample of the 57% EC formulation showed no prominent exotherms or endotherms. However, a marked decomposition process occurred from about 338°C and on to the instrument limit of 400°C. This decomposition process was substantiated by the slow weight loss observed from the TGA data as temperature increased. At about 700°C, almost 80% of the original weight was gone. From 700 to 1000°C, another 10% of the original weight disappeared.

Kennedy et al.[13] also conducted DTA on malathion. Based on their laboratory analyses, Kennedy et al. concluded that the temperatures of complete combustion of the malathion reference standard and the 57% liquid formulation were 663°C (1225°F) and 715°C (1319°F), respectively.

A total of 11 tests were conducted using the 57% malathion EC formulation; the results of these tests are summarized in Table 9.

Initially, nine tests were made using the EC formulation (Runs Nos. 1 through 9). Neither malathion nor any other sulfur containing organic phosphates were detected at Sample Point No. ② (the incinerator offgas) for any of these experiments. (The values given in Table 9 are the detection limits for malathion in the respective samples.) Further, neither malathion nor any other sulfur-containing phosphates were detected at any other point in the experimental system except at Sample Point No. ① (the incinerator feed).

Relatively high quantities of total pyrophosphates, however, were detected in the incinerator effluent from those runs using concentrated feed (350 to 590 mg malathion per milliliter) (Runs Nos. 5 through 9).

Two additional tests (Runs Nos. 10 and 11) were then made using lower concentrations of malathion. As had been the case with Runs Nos. 1 through 9, no malathion was detected in the incinerator effluent. Runs Nos. 10 and 11, however, failed to parallel earlier results in which detectable levels of total pyrophosphates were found only in tests in which relatively high concentrations of malathion (350 to 590 mg/ml) were burned. Thus, a definite correlation could not be made between total pyrophosphate generation and either operating temperature or incinerator feed concentration.

In order to evaluate the effect of physical form on the efficiency with which malathion can be incinerated, five tests were made using an ~ 25% dust formulation. Results from these experiments are summarized in Table 10. Two efficiencies of combustion have been calculated. The first considered only the potential quantity of malathion (based on its detection limit) in the incinerator input and discharge. This efficiency calculation showed that > 99.99% of the malathion injected into the incinerator was at least partially degraded at all temperatures tested.

Table 9. SUMMARY OF TEST RESULTS--57% MALATHION EC FORMULATION

Run No.	Malathion rate g/hr (lb/hr)	Primary chamber temperature °C (°F)	Excess air %	Retention time sec		Ratio of malathion in the off-gas to malathion fed	Ratio of total species content of the off-gas to malathion fed	Incinerator efficiency %	
				Primary chamber	Second chamber			Malathion	Total species
1	1,760 (3.89)	1050 (1930)	130	2.2	2.2	$< 1.9 \times 10^{-5}$	$< 6 \times 10^{-5}$	> 99.99	> 99.99
2	2,630 (5.80)	1060 (1940)	74	3.6	3.7	$< 5 \times 10^{-6}$	$< 3 \times 10^{-5}$	> 99.99	> 99.99
3	1,470 (3.24)	1000 (1840)	44	4.8	5.0	$< 8 \times 10^{-6}$	$< 2 \times 10^{-5}$	> 99.99	> 99.99
4	930 (2.04)	1080 (1980)	122	2.2	2.6	$< 2.6 \times 10^{-5}$	$< 5 \times 10^{-5}$	> 99.99	> 99.99
5	1,170 (2.58)	620 (1140)	176	6.8	6.5	$< 1 \times 10^{-5}$	$< 3 \times 10^{-5}$	> 99.99	> 99.99
6	1,970 (4.35)	640 (1190)	188	6.6	6.5	$< 6 \times 10^{-6}$	$< 1 \times 10^{-5}$	> 99.99	> 99.99
7	1,990 (4.38)	690 (1270)	114	6.2	6.2	$< 6 \times 10^{-6}$	$< 1 \times 10^{-5}$	> 99.99	> 99.99
8	1,650 (3.62)	700 (1290)	114	6.0	6.1	$< 8 \times 10^{-6}$	$< 2 \times 10^{-5}$	> 99.99	> 99.99
9	3,630 (8.00)	960 (1760)	95	3.9	3.9	$< 4 \times 10^{-6}$	$< 9 \times 10^{-6}$	> 99.99	> 99.99
10	660 (1.45)	620 (1150)	197	5.1	5.1	$< 3 \times 10^{-5}$	$< 5 \times 10^{-5}$	> 99.99	> 99.99
11	630 (1.39)	600 (1110)	311	4.5	4.3	$< 3.2 \times 10^{-5}$	$< 6 \times 10^{-5}$	> 99.99	> 99.99

Table 10. SUMMARY OF TEST RESULTS--25% MALATHION WP FORMULATION

Run No.	Malathion rate g/hr (lb/hr)	Primary chamber temperature °C (°F)	Excess air %	Retention time sec		Particulate loading mg/m^3 (gr/dscf)	Ratio of malathion in the off-gas to malathion fed	Ratio of total species content of the off-gas to malathion fed	Incineration efficiency %	
				Primary chamber	Second chamber				Malathion	Total species
A	3,310 (7.33)	810 (1490)	43	6.2	4.5	37,000 (16.1)	$< 6.5 \times 10^{-7}$	$< 6.5 \times 10^{-7}$	> 99.99	> 99.99
B	4,580 (10.08)	1060 (1900)	37	3.8	3.9	36,800 (16.0)	6.6×10^{-7}	6.6×10^{-7}	> 99.99	> 99.99
C	3,130 (6.90)	730 (1340)	113	5.7	5.6	35,100 (15.2)	$< 6.8 \times 10^{-7}$	$< 1.2 \times 10^{-5}$	> 99.99	> 99.99
D	3,290 (7.25)	930 (1710)	136	1.9	1.8	29,300 (12.7)	$< 6.3 \times 10^{-7}$	2.4×10^{-6}	> 99.99	> 99.99
E	1,100 (2.42)	630 (1170)	157	6.2	6.0	26,900 (11.7)	$< 1.4 \times 10^{-6}$	$< 1.6 \times 10^{-6}$	> 99.99	> 99.99

The second efficiency calculation included not only the malathion that was left, but also all other organic phosphate species detected. Using this calculation, all five tests showed an efficiency of > 99.99% for the incinerator effluent gas.

Particulate loading for all five tests exceeded established emission rates, indicating the need for a particulate control device when incinerating malathion dust formulations.

Minor operating problems were encountered during the 57% malathion EC tests. Plugging of the demister in the first stage water scrubber was observed, primarily during tests conducted at low draft. In addition, a visible white plume was noted emitting from the scrubber system exhaust. These same problems, i.e., inability to remove P_2O_5 from the effluent gas stream and plugging of filter elements, had also been encountered during recent studies of the incineration of organophosphorus chemical warfare agents.[23]

Toxaphene

DTA of technical grade toxaphene showed no prominent endotherm or exotherm at lower temperatures. However, as the temperature reached about 290°C, sharp decomposition was observed and continued to 400°C (instrument limit). This decomposition process was substantiated by the TGA data which indicated almost 95% of the initial weight was lost when the temperature reached 300°C.

DTA and TGA of the 20% toxaphene dust formulation indicated a slow decomposition process, while TGA indicated slow weight loss all the way to about 700°C. The weight loss took place mainly at two temperature ranges, one quite abruptly at about 190 to 260°C (about 20% weight loss). At 710°C about 35% of the original weight was gone, compared to the nominal 20% toxaphene content of the formulation. No further weight loss was observed from 710 to 1000°C.

DTA of a sample of recrystallized toxaphene obtained by evaporation of a sample of the 60% EC formulation showed an endotherm at about 306°C, which may have been only a phase change; TGA data showed no significant weight loss at this temperature. However, prior to this endotherm, decomposition was observed which was substantiated by the abrupt weight loss from 180 to 280°C in the TGA. About 95% of the original weight was gone at 280°C. Essentially no more than 3% additional weight loss was observed from 280 to 1000°C.

Eleven tests were made using the 60% EC toxaphene formulation. The temperature of the primary chamber was varied between the lower operating limit of the incinerator, i.e., ~ 650°C (1200°F), and 1000°C (1830°F).

The results of these 11 tests are shown in Table 11. Because technical grade toxaphene consists of a number of chlorinated hydrocarbons (including at least 175 polychlorinated 10-carbon compounds), the efficiency of toxaphene incineration was evaluated based on actual toxaphene content of the incinerator feed (Sample Point No. ①), versus the total chlorinated hydrocarbon species detected in the incinerator effluent (Sample Point No. ②). The percent efficiency calculations showed that > 99.99% of the toxaphene injected into the incinerator was degraded for all 11 experiments, i.e., over the ranges of excess air, operating temperature, and incinerator feed rate investigated.

There was no correlation between operating temperature and the relative amount of unburned "toxaphene" discharged (as shown by the "Ratio of Chlorinated Hydrocarbon Content of the Off-Gas to Toxaphene Fed" column of Table 11). Significantly higher levels were discharged, however, from Runs Nos. 5 and 7. These two tests also had the shortest retention times in the primary chamber (2.4 and 2.2 sec, respectively).

Six tests were made using an ~ 20% dust formulation of toxaphene in order to evaluate the effect of physical form on incineration efficiency. The results of the six tests are summarized in Table 12. The efficiency of toxaphene incineration for all six tests was > 99.99%.

The particulate loadings for the toxaphene dust experiments followed the previously established trend of high particulate emission levels for dust formulations. The incineration of toxaphene dust formulation would therefore require a particulate emissions control system.

Operating difficulties were encountered on all four dust tests made at the higher temperature of ~ 1000°C (1830°F), i.e., Runs Nos. C through F. In fact, Run No. C was terminated when only half completed (30 min of sampling) because of loss of draft within the incinerator. Inspection of the incinerator disclosed that the six 11.4 cm x 11.4 cm (4-1/2 in x 4-1/2 in.) openings in the wall between the primary and secondary chamber (see Figure 2, p. 22) had been completely plugged. The interior of the "plugged incinerator" is shown in Figure 44, p. 249.

Feeding problems were also encountered with the toxaphene dust. The dust tended to bridge in the feed line to the injection nozzle.

Table 11. SUMMARY OF TEST RESULTS--60% TOXAPHENE EC FORMULATION

Run No.	Toxaphene rate g/hr (lb/hr)	Primary chamber temperature °C (°F)	Excess air %	Retention time sec		Ratio of chlorinated hydrocarbon content of the off-gas to toxaphene fed	Efficiency %
				Primary chamber	Second chamber		
1	1,250 (2.75)	620 (1150)	349	5.3	4.9	3×10^{-6}	> 99.99
2	1,220 (2.70)	630 (1160)	198	5.0	4.6	2×10^{-6}	> 99.99
3	1,540 (3.40)	680 (1260)	160	4.6	4.4	9×10^{-7}	> 99.99
4	1,520 (3.35)	1040 (1900)	47	3.4	3.5	3×10^{-7}	> 99.99
5	1,250 (2.75)	980 (1800)	124	2.4	2.4	3.3×10^{-5}	> 99.99
6	3,240 (7.15)	1040 (1900)	71	3.8	3.9	2×10^{-8}	> 99.99
7	2,340 (5.15)	990 (1820)	128	2.2	2.2	1.7×10^{-5}	> 99.99
8	2,220 (4.90)	670 (1240)	212	5.2	5.1	4×10^{-6}	> 99.99
9	1,090 (2.40)	660 (1220)	154	6.6	6.2	9×10^{-9}	> 99.99
10	2,110 (2.65)	680 (1260)	228	6.5	6.4	2×10^{-6}	> 99.99
11	1,070 (2.35)	650 (1200)	150	6.7	6.5	1×10^{-8}	> 99.99

Table 12. SUMMARY OF TEST RESULTS--20% TOXAPHENE DUST FORMULATION

Run No.	Toxaphene rate g/hr (lb/hr)	Primary chamber temperature °C (°F)	Excess air %	Retention time sec		Particulate loading mg/m^3 (gr/dscf)	Ratio of total chlorinated hydrocarbons in the off-gas to total toxaphene fed	Incineration efficiency %
				Primary chamber	Second chamber			
A	3,520 (7.76)	670 (1240)	94	7.7	8.3	73,000 (31.2)	3.1×10^{-6}	> 99.99
B	2,750 (6.06)	670 (1240)	166	5.3	5.7	37,000 (16.1)	2.0×10^{-6}	> 99.99
C	3,060 (6.75)	1010 (1850)	53	2.9	3.2	4,620 (2.01)	3.6×10^{-5}	> 99.99
D	3,850 (8.49)	1030 (1880)	44	3.4	4.1	7,900 (3.43)	1.8×10^{-6}	> 99.99
E	3,430 (7.56)	970 (1770)	122	2.5	2.8	2,640 (1.15)	1.6×10^{-6}	> 99.99
F	3,310 (7.30)	1010 (1850)	121	2.4	2.8	7,900 (3.43)	3.0×10^{-5}	> 99.99

Bridging problems have been encountered by others in formulation of dusts using the same attapulgite clay as was used for the toxaphene dust formulation tested. Grounding of the screens used in the formulation process reported overcame the difficulty, indicating that a static electrical charge on the dust particles was the cause.

Atrazine

DTA of technical grade atrazine (conducted on an instrument having a higher temperature limit than had previously been used) showed that decomposition of the compound started at about 180°C with two distinct endotherms at 185 and 240°C, and exotherms at about 350, 450, and 470°C. The decomposition process are substantiated by TGA data which indicated that almost 95% of the sample weight was lost at about 300°C, and at about 600°C, no sample was left.

DTA and TGA were also made of an atrazine sample obtained by evaporation of a sample of a 4 lb/gal liquid formulation. DTA data showed that as temperature increased, decomposition of the sample started, and at about 185 and 245°C, two prominent endotherms were observed. As temperature reached 350 and 440°C, distinct exotherms were observed. The decomposition process was again substantiated by the TGA data which show that from 200 to 220°C about 90% of the sample was lost, and at about 600°C, practically all the sample was gone.

DTA data for the 80% wettable powder atrazine formulation showed endotherms and exotherms in addition to those observed from the technical material. These endotherms and exotherms could well be attributed to the additives in the formulation. Decomposition was completed at about 600°C, as substantiated by TGA data which show that at 600°C over 90% of the sample was gone.

Kennedy et al.[13/] also conducted DTA analysis of atrazine. Based on their analyses, Kennedy et al. concluded that the temperatures of complete combustion of the atrazine reference standard and an 80% wettable powder formulation were 650°C (1202°F) and 600°C (1112°F), respectively.

Nine tests were conducted using the 4 lb/gal liquid formulation of atrazine. Nominal operating conditions for these tests were "high" and "low" feed rates [3.40 kg (7.5 lb) and 1.70 kg (3.75 lb) active ingredient per hour], excess air rates (150 and 50%), and operating temperatures of 1000°C (1830°F) and 650°C (1200°F).

Liquid atrazine, like the water based picloram formulation, was not miscible with No. 2 fuel oil and therefore, was pumped into the incinerator using a separate injector system. The liquid atrazine injector system utilized a standard fuel oil burner nozzle of the appropriate size, and the nozzle adapter and oil pipe from a fuel oil burner. Preliminary tests, however, showed that the liquid atrazine would plug the nozzle and nozzle adapter almost immediately after insertion into the incineration chamber. For this reason, the nozzle adapter was modified so that it would be cooled by the water-jacketed injection nozzle used for dust injection (see Figure 52, p. 266). This modification eliminated the problem of plugging during the test period.

Results of tests using the 4 lb/gal liquid formulation are given in Table 13. Two efficiencies of combustion were calculated for the atrazine liquid tests. The first was based on atrazine only, while the second included consideration of all nitrogenous organic species (including atrazine) detected in the effluent gas. Both of these efficiencies were > 99.99% for all tests. Thus, the efficiency of liquid atrazine incineration was found to be > 99.99% over the temperature range of 550°C (1030°F) to 1040°C (1900°F).

The relative quantity of atrazine (and total nitrogenous organic species) not decomposed, however, does appear to be related to operating temperature. The highest quantity of atrazine (and total nitrogenous organic species) as shown in Columns 7 and 8, respectively, of Table 13, was emitted from Run No. 6 which was conducted at the lowest primary chamber temperature (550°C) and 7.8 sec. The lowest quantities detected were from Run No. 9, which was conducted at the highest temperature (1040°C) and 2.7 sec.

Five additional tests were made using an 80% wettable powder formulation of atrazine in order to determine the effect of physical form on efficiency. Operational data and analytical results for the ~ 80% atrazine wettable powder formulation tests are summarized in Table 14. The results of these five tests parallel those of the nine tests using the liquid atrazine formulation. Both efficiencies for all five tests were > 99.99%.

Incineration of atrazine at the lower temperatures, ~ 650°C (1200°F), yielded high levels of cyanide (CN^-) in the effluent, i.e., 198 to 5,740 mg/m^3. The higher temperatures, ~ 1000°C (1830°F), generally yielded much lower concentrations. However, only those tests conducted at the higher temperatures and relatively high excess air rates (> 75%) routinely yield concentrations of < 1 mg/m^3. Thus, temperatures of about 1000°C (1830°F), for 2 sec retention time and excess air of > 75% are required to incinerate atrazine and obtain cyanide concentration in the undiluted off-gas of < 1 mg/m^3.

Table 13. SUMMARY OF TEST RESULTS--4 LB/GAL ATRAZINE LIQUID FORMULATION

Run No.	Atrazine rate g/hr (lb/hr)	Primary chamber temperature °C (°F)	Excess air %	Retention time sec		Ratio of atrazine in off-gas to atrazine fed	Ratio of total species content of off-gas to atrazine fed	Incineration efficiency %	
				Primary chamber	Second chamber			Atrazine	Total species
1	1,470 (3.25)	1020 (1860)	79	2.6	2.5	$< 1.1 \times 10^{-5}$	$< 2.6 \times 10^{-5}$	> 99.99	> 99.99
2	1,470 (3.25)	1020 (1860)	123	2.1	2.0	$< 1.1 \times 10^{-5}$	$< 2.1 \times 10^{-5}$	> 99.99	> 99.99
3	1,320 (2.92)	730 (1340)	138	4.0	3.6	$< 8 \times 10^{-6}$	$< 4 \times 10^{-5}$	> 99.99	> 99.99
4	1,600 (3.52)	700 (1290)	90	5.0	4.6	$< 6 \times 10^{-6}$	$< 3 \times 10^{-5}$	> 99.99	> 99.99
5	3,420 (7.54)	970 (1780)	76	2.0	1.8	$< 9 \times 10^{-6}$	$< 5 \times 10^{-5}$	> 99.99	> 99.99
6	3,410 (7.51)	550 (1030)	93	7.8	6.9	$< 5 \times 10^{-5}$	$< 7 \times 10^{-5}$	> 99.99	> 99.99
7	4,470 (9.85)	700 (1300)	143	3.6	3.3	$< 2.9 \times 10^{-6}$	$< 6 \times 10^{-6}$	> 99.99	> 99.99
8	3,290 (7.25)	940 (1720)	140	1.6	1.3	$< 9 \times 10^{-6}$	$< 2.5 \times 10^{-5}$	> 99.99	> 99.99
9	1,480 (3.26)	1040 (1900)	52	2.7	2.8	$< 8 \times 10^{-6}$	$< 1.6 \times 10^{-5}$	> 99.99	> 99.99

Table 14. SUMMARY OF TEST RESULTS--80% ATRAZINE WP FORMULATION

Run No.	Atrazine rate g/hr (lb/hr)	Primary chamber temperature °C (°F)	Excess air %	Retention time sec Primary chamber	Retention time sec Second chamber	Particulate loading mg/m^3 (gr/dscf)	Ratio of atrazine in off-gas to total atrazine fed	Ratio of total species in off-gas to total atrazine fed	Incineration efficiency % Atrazine	Incineration efficiency % Total species
A	2,630 (5.8)	1070 (1960)	43	2.7	2.8	2,060 (0.89)	4.6×10^{-7}	5×10^{-7}	> 99.99	> 99.99
B	3,080 (6.8)	970 (1770)	125	2.2	3.9	1,750 (0.76)	1.8×10^{-7}	6×10^{-7}	> 99.99	> 99.99
C	2,130 (4.7)	600 (1120)	146	5.6	5.2	4,700 (2.04)	2.5×10^{-7}	1.1×10^{-6}	> 99.99	> 99.99
D	2,590 (5.7)	970 (1780)	71	2.7	3.8	3,790 (1.64)	3.0×10^{-7}	8×10^{-7}	> 99.99	> 99.99
E	3,220 (7.1)	650 (1200)	111	6.8	6.4	7,500 (3.26)	3×10^{-8}	3×10^{-7}	> 99.99	> 99.99

The particulate loadings for the wettable powder formulation of atrazine followed the previous trend, although not as high, of particulate emission levels which exceed established limits. The incineration of atrazine wettable powder formulations would require a particulate emissions control system.

The only operational problem encountered with atrazine incineration was the plugging of the liquid formulation injection nozzle. Insulation of this nozzle with the water jacketed dust nozzle, as discussed above, overcame this problem.

The high concentration of active ingredients in the dust formulation (80%) made the desired active ingredient injection rate more difficult to attain.

Captan

DTA of technical grade captan showed a distinct endotherm at about 185°C which approximately corresponds to the reported melting point of pure captan (m.p. range 172 to 178°C). In additon, the data showed two distinct exotherms at about 250 and 550°C, indicating decomposition of the compound. The decomposition process was substantiated by the TGA data which indicated that about 75% of the compound is lost at about 250°C, and almost all of the compound is lost at 600°C.

DTA and TGA were also conducted on a 50% captan wettable powder formulation. DTA data of this powder formulation showed a pattern of endotherm and exotherms similar to that of technical captan, i.e., an endotherm at about 185°C (indicating possible melting), and two exotherms at about 220 and 530°C, respectively (indicating decomposition). The decomposition process was again substantiated by the TGA data which indicated approximately 50% lost in sample weight at 250°C and 60% loss at the completion of the experiment (at 1000°C). The weight loss due to decomposition corresponded (within experimental error) to the amount of captan (50%) in the formulation.

Eight tests were made using the 50% captan wettable powder formulation. The results of these tests are summarized in Table 15. The efficiency of combustion was > 99.99% for all eight tests, whether based on captan or total chlorinated species detected in the off-gas and incinerator residues. No correlation was found between the relative rate of captan and total chlorinated species in the incinerator off-gas and specific operating conditions.

Table 15. SUMMARY OF TEST RESULTS--50% CAPTAN WP FORMULATION

Run No.	Captan rate g/hr (lb/hr)	Primary chamber temperature °C (°F)	Excess air %	Retention time sec Primary chamber	Retention time sec Second chamber	Particulate loading mg/m^3 (gr/dscf)	Ratio of captan in off-gas to total captan fed	Ratio of total species in off-gas to total captan fed	Incineration efficiency % Captan	Incineration efficiency % Total species
A	2,880 (6.35)	1000 (1830)	137	1.8	1.8	8,500 (3.7)	$< 2.6 \times 10^{-7}$	$< 1.4 \times 10^{-6}$	> 99.99	> 99.99
B	2,850 (6.28)	920 (1690)	94	3.2	3.2	14,500 (6.3)	$< 9 \times 10^{-8}$	$< 1.7 \times 10^{-6}$	> 99.99	> 99.99
C	1,640 (3.62)	1010 (1850)	76	2.5	2.5	4,800 (2.08)	$< 8 \times 10^{-9}$	$< 1.2 \times 10^{-6}$	> 99.99	> 99.99
D	1,110 (2.45)	980 (1790)	135	2.0	1.9	6,500 (2.82)	2.2×10^{-8}	1.1×10^{-6}	> 99.99	> 99.99
E	1,250 (2.76)	660 (1220)	192	4.2	3.9	14,100 (6.1)	$< 2.6 \times 10^{-8}$	$< 2.0 \times 10^{-6}$	> 99.99	> 99.99
F	1,410 (3.11)	670 (1230)	130	5.3	5.1	16,100 (7.0)	$< 1.6 \times 10^{-9}$	$< 3.8 \times 10^{-6}$	> 99.99	> 99.99
G	2,230 (4.92)	650 (1200)	252	6.8	6.6	65,000 (28)	3×10^{-7}	1×10^{-6}	> 99.99	> 99.99
H	2,040 (4.50)	690 (1280)	99	6.7	6.5	31,600 (13.7)	$< 5 \times 10^{-9}$	$< 3 \times 10^{-7}$	> 99.99	> 99.99

Analysis of the off-gas for cyanide (CN^-) content showed that significant concentrations (and amounts) were generated on all tests (27 to 133 mg/m^3). No correlation has been found between the relative rate of cyanide generation (rate of cyanide generated to rate of captan incinerated) and any of the operating variables being investigated (rate of pesticide injection, percent excess air, and operating temperature).

Particulate loadings for all seven wettable powder tests were above established limits. Particulate emission control devices would be required for captan incineration.

No operational problems were encountered during the incineration of captan. However, an H_2S-like odor was quite evident during experimental runs.

Zineb

DTA data for technical grade (85%) zineb showed that decomposition of the sample started at about 150°C, with two endotherms at about 160 and 290°C, and exotherms at about 190, 440, 530, and 600°C. The decomposition process was substantiated by the TGA data which indicate that about 80% of the sample weight is lost at 800°C.

DTA data for the 75% zineb wettable powder formulation showed a decomposition pattern similar to that of the technical grade zineb, with characteristic endotherms at 170 and 260°C, and exotherms at 200, 440, 530, and 610°C. The decomposition process was substantiated by the TGA data which indicated that about 75% of the sample weight is lost at 800°C.

Kennedy et al. (1969)[13] also conducted DTA analysis of zineb and based on their laboratory analyses, they concluded that the temperatures of complete combustion of the zineb reference standard and the 75% wettable powder formulation were 840°C (1544°F) and 690°C (1274°F), rerespectively.

A total of 11 tests were conducted using the 75% zineb wettable powder. The results of these tests are given in Table 16.

The zineb analyses, however, are not comparable to those of the eight other pesticides tested because of limitations in the available zineb analytical methods and the inability to analyze the filter element of the off-gas sampling train (see Appendix B, p. 113). However, an approximation of the zineb content of the particulates trapped on the filter element was made by utilizing the analyses for other residue samples obtained after the completion of each test. These additional

Table 16. SUMMARY OF TEST RESULTS--75% ZINEB WP FORMULATION

Run No.	Zineb rate g/hr (lb/hr)	Primary chamber temperature °C (°F)	Excess air %	Retention time, sec Primary chamber	Retention time, sec Second chamber	Particulate loading mg/m^3 (gr/dscf)	Approximate ratio of zineb in off-gas to zineb fed	Incineration efficiency %
A	3540 (7.8)	890 (1630)	69	3.3	3.3	13,200 (5.7)	4×10^{-5}	> 99.99
B	3180 (7.0)	970 (1770)	106	1.9	1.9	9,400 (4.1)	3×10^{-5}	> 99.99
C	3220 (7.1)	680 (1260)	102	5.2	5.1	15,400 (6.7)	3×10^{-5}	> 99.99
D	2540 (5.6)	710 (1310)	153	3.4	3.2	14,800 (6.4)	3×10^{-5}	> 99.99
E	1590 (3.5)	690 (1270)	111	5.0	4.8	7,200 (3.12)	3×10^{-5}	> 99.99
F	1720 (3.8)	650 (1200)	105	4.4	4.2	13,600 (5.9)	3×10^{-5}	> 99.99
G	1680 (3.7)	980 (1790)	67	2.5	2.6	7,200 (3.12)	4×10^{-7}	> 99.99
H	1720 (3.8)	940 (1730)	131	1.8	1.7	8,400 (3.6)	4×10^{-7}	> 99.91
I	3040 (6.7)	1000 (1830)	62	2.4	2.3	10,600 (4.6)	3×10^{-6}	> 99.99
J	3580 (7.9)	930 (1710)	120	1.9	1.7	11,100 (4.8)	1×10^{-5}	> 99.99
K	2130 (4.7)	710 (1310)	85	5.1	4.9	13,700 (5.9)	1×10^{-6}	> 99.99

samples were obtained from the walls of the horizontal and vertical sections of the incinerator stack preceding Sample Point No. ②, the normal incinerator off-gas sampling point. Using this approximation, efficiencies of combustion have been calculated as > 99.99% for all 11 tests.

High cyanide (CN^-) levels were detected in the incinerator off-gas for all zineb tests ranging in concentration from 138 to 1,260 mg/m^3.

The particulate loadings for zineb all exceed what can be considered low emissions and indicate the need for particulate control devices when zineb wettable powder formulations are incinerated.

The most significant operational problem with the zineb incineration was the inability of the off-gas scrubber system to clean up the effluent gas. A white plume was discharged from the scrubber system exhaust, the opacity of which ranged from 0 to 45%. The particulate material was also deposited on interior surface areas throughout the scrubber system. Residue deposition inside the scrubber system blower caused blower vibration during latter tests. (See Figure 61, p. 317.)

The deposition of particulate material also caused plugging of the demister pads in the first and second stage scrubbers. The demister pad was removed from the second stage (hexylene glycol) scrubber after Run No. E in order to reduce plugging of the system.

The odor of SO_2 was also noted during the incineration of zineb (SO_2 levels in the incinerator off-gas ranged from 6,670 to 22,900 mg/m^3).

Mirex

DTA and TGA were made of technical grade mirex (97%). DTA data showed that decomposition started at about 130°C, with two endotherms at about 140° and 370°C, respectively, and an exotherm at about 570°C. The decomposition process was substantiated by the TGA data which indicated that about 95% of the sample weight was lost at about 350°C, and almost all the sample was gone at 800°C.

No DTA and TGA experiments were performed on the bait formulation tested because of the small amount of mirex present (0.3% mirex on ground corncob grit).

Ten tests were made using an 0.3% mirex bait formulation. Because of the size of the incinerator [designed for 45.4 kg/hr (100 lb/hr) of Type 1 waste, equivalent to 6.86×10^8 J/hr (650,000 Btu/hr)], the heat of combustion of the mirex bait formulation 2.168×10^7 J/kg (9,329 Btu/lb), and the low concentration of mirex (~ 0.3%), low rates of active ingredient injection were used. Mirex (as the pure active ingredient) was injected at nominal rates of 68 g/hr (0.15 lb/hr) and 34 g/hr (0.075 lb/hr), rather than the 3.40 kg/hr (7.5 lb/hr) and 1.70 kg/hr (3.75 lb/hr) rates used for all other pesticides studied.

The operational data for these 10 tests are summarized in Table 17. Two efficiencies were calculated for the incineration of mirex, based on (a) the mirex content of the effluent gas and solid residues, and (b) the total chlorinated organic species (mirex plus all other chlorinated organic species) detected in the effluent gas and solid residues. Efficiency based on mirex content only ranged from > 98.21 to > 99.98%, while efficiency based on total chlorinated organic species detected ranged from > 97.78 to > 99.96%. Both of these ranges were significantly lower than those for the other pesticides studied.

Additional samples were taken during the mirex tests using a special sampler designed to catch the mirex bait particles as they fell through the combustion chamber in order to approximate the degree of decomposition occurring during the first few seconds.

The average mirex content of the bait formulation used for these tests was 2,710 ppm (based on 17 samples, ranging from 1,940 to 4,130 ppm) while the average conentration of mirex in the "grab" sample was 770 ppm. Although the data showed no strong correlation with any particular operating condition, they did indicate that a substantial portion of the mirex (> 70%) was "removed" from the bait formulation during the first 2 sec residence in the primary chamber. These results parallel those from grab sampling of picloram pellets, and reiterate the need to insure adequate retention of solid residues in the primary combustion chamber.

The test data did not show what operating conditions would be required to effect mirex decomposition comparable to that which has been achieved for the other pesticides studied (i.e., an incineration efficiency of > 99.99%). Either higher temperatures than those investigated with the appropriate retention time or secondary combustion (or possibly both) would be required.

The particulate loadings for four of the mirex tests were within the established limit, while the other six were of the same order of magnitude. Thus, it appears that the 0.3% mirex bait formulation when incinerated to an acceptable level (> 99.99% destruction) would not require particulate control devices.

Table 17. SUMMARY OF TEST RESULTS--0.3% MIREX BAIT FORMULATION

Run No.	Contained mirex g/hr	Primary chamber temperature °C (°F)	Excess air %	Retention time sec Primary chamber	Retention time sec Second chamber	Particulate loading mg/m^3 (gr/dscf)	Ratio of mirex in off-gas to total mirex fed	Ratio of total species in the off-gas to total mirex fed	Incinerator efficiency % Mirex	Incinerator efficiency % Total species
A	72	900 (1650)	57	2.5	3.0	426 (0.195)	1.0×10^{-6}	1.3×10^{-2}	> 99.99	> 98.70
B	70	870 (1600)	85	2.4	2.8	222 (0.096)	3.6×10^{-6}	5×10^{-4}	> 99.96	> 99.94
C	69	930 (1710)	82	2.0	2.0	213 (0.092)	3.3×10^{-6}	8×10^{-5}	> 99.96	> 99.91
D	32	590 (1090)	225	2.8	3.4	570 (0.247)	1.8×10^{-2}	2.2×10^{-2}	> 98.21	> 97.78
E	31	700 (1290)	78	6.0	6.2	205 (0.089)	2.9×10^{-3}	5×10^{-3}	> 99.70	> 99.50
F	33	820 (1510)	46	5.3	5.5	251 (0.109)	8×10^{-4}	2.4×10^{-3}	> 99.91	> 99.75
G	35	940 (1730)	116	2.0	2.0	168 (0.073)	1.2×10^{-3}	3.1×10^{-3}	> 99.87	> 99.68
H	70	880 (1620)	123	1.7	1.6	180 (0.078)	1.6×10^{-4}	5×10^{-4}	> 99.98	> 99.93
I	68	760 (1400)	149	2.2	2.3	179 (0.078)	1.2×10^{-3}	1.4×10^{-3}	> 99.88	> 99.85
J	33	920 (1690)	161	1.8	1.5	150 (0.065)	2.3×10^{-4}	3.9×10^{-4}	99.97	99.96

There were no specific operational problems with mirex. The fact that the mirex bait was formulated on a combustible inert carrier, however, resulted in the continued burning of the solid residue in the bottom of the primary combustion chamber throughout the experiments.

GENERAL FINDINGS

The efficiency of pesticide combustion was generally uniformly high over the complete ranges of operating conditions investigated. The only exception, as noted above, was the 0.3% mirex bait formulation.

The mirex bait experiments differed from all other tests in that this was the only formulation tested that contained a combustible material as the inert carrier, the active ingredient content was low (0.3% versus 10 to 80% for the other formulations tested), and a lower range of primary chamber temperatures was evaluated.

The particulate emissions from the solid formulations tested (i.e., pellets, granules, wettable powders, and dusts) were generally higher than the standards established for large (≥ 4.5 x 10^4 kg/day (50 tons/day)), new emission sources. Thus, the incineration of the major pesticide formulations will require particulate control devices if these emission standards are to be met.

Odors were frequently detected during the tests, even though the efficiency of incineration was quite high. This potential problem area exists whenever sulfur-containing pesticides are being incinerated.

Visible plumes were discharged from the experimental apparatus during the incineration of picloram, malathion, and zineb; e.g., after the off-gas had been scrubbed by a three stage scrubber system. Experiments during which such plumes were discharged also generally involved difficulty in operating the scrubber systems due to particulate buildup (plugging) of the three demister pads in the three scrubbers.

Detectable levels of cyanide (as CN^-) were found in the incinerator off-gas during tests with all four of the nitrogen-containing pesticides studied (picloram, atrazine, captan, and zineb).

The available methods for specific pesticide analysis pose major limitations on the type and significance of data that can be obtained regarding pesticide incineration. For many pesticides (such as the chlorinated hydrocarbons DDT and aldrin), and the organic phosphate (malathion), adequate techniques are available for quantification and identification of the active ingredient and related compounds in the incinerator off-gas and residues. For other pesticides, such as zineb, the only techniques available are either not applicable to the residue matrix, or are based on the analysis of certain degradation products rather than on the active ingredient.

SYSTEM PERFORMANCE

The experimental apparatus used to conduct the tests discussed above functioned satisfactorily throughout the course of the study.

Minor modifications of the pesticide feed system were required in order to inject water-based formulations. This modification included a separate injection system for the pesticide formulation, consisting of a water jacketed fuel oil burner nozzle of the appropriate size and an adequate pump.

High pressure drops were encountered across the demister pads of the first two scrubbers during some of the experiments. This operational problem was generally encountered when operating at low incinerator feed rates and draft.

Extensive corrosion was noted during the course of the study. Most seriously affected, as one would expect, were the internal and ancillary piping of the first stage water scrubber. The entire first scrubber was rebuilt (replaced) near the midpoint of the experimental phase of the study. The demister pad (constructed of 304 stainless steel) and the reducer cone on the first stage scrubber influent line were replaced twice during the study. The most extensive corrosion appeared to result from the DDT and toxaphene experiments.

PROBLEM AREAS

The major problem in the operation of the experimental facility was associated with its operation at lower than design rates. As was discussed in some detail in the subsection entitled Experimental Facilities, page 20, the experimental incinerator was designed to operate at 45.4 kg/hr (100 lb/hr) of Type 1 waste (equivalent to 6.86×10^8 J/hr (650,000 Btu/hr)), which corresponds to a No. 2 fuel oil firing rate of approximately 23 liters/hr (6 gal/hr). Most of the experiments conducted subsequent to the DDT tests were conducted at 20 to 50% of this design rate in order to obtain lower primary chamber temperatures.

These low rates tended to amplify operational difficulties that would have been less acute at design conditions, e.g., the plugging of the scrubber demister pads while operating at low draft.

The removal of solid residue from the primary chamber after aldrin granule and picloram pellet tests conducted at high temperature (~ 1000°C) caused minor problems. A major portion of the front wall of the primary combustion chamber had to be removed after each test in order to provide adequate access for removal of the hardened residue.

Large quantities of solid residue accumulated in the long horizontal section of the incinerator stack (see Figure 1, p. 21), which necessitated its frequent dismounting and cleanout. These deposits were particularly heavy after tests with solid formulations containing low concentrations of active ingredients, i.e., the 10% DDT dust and the 20% toxaphene dust.

SECTION VI

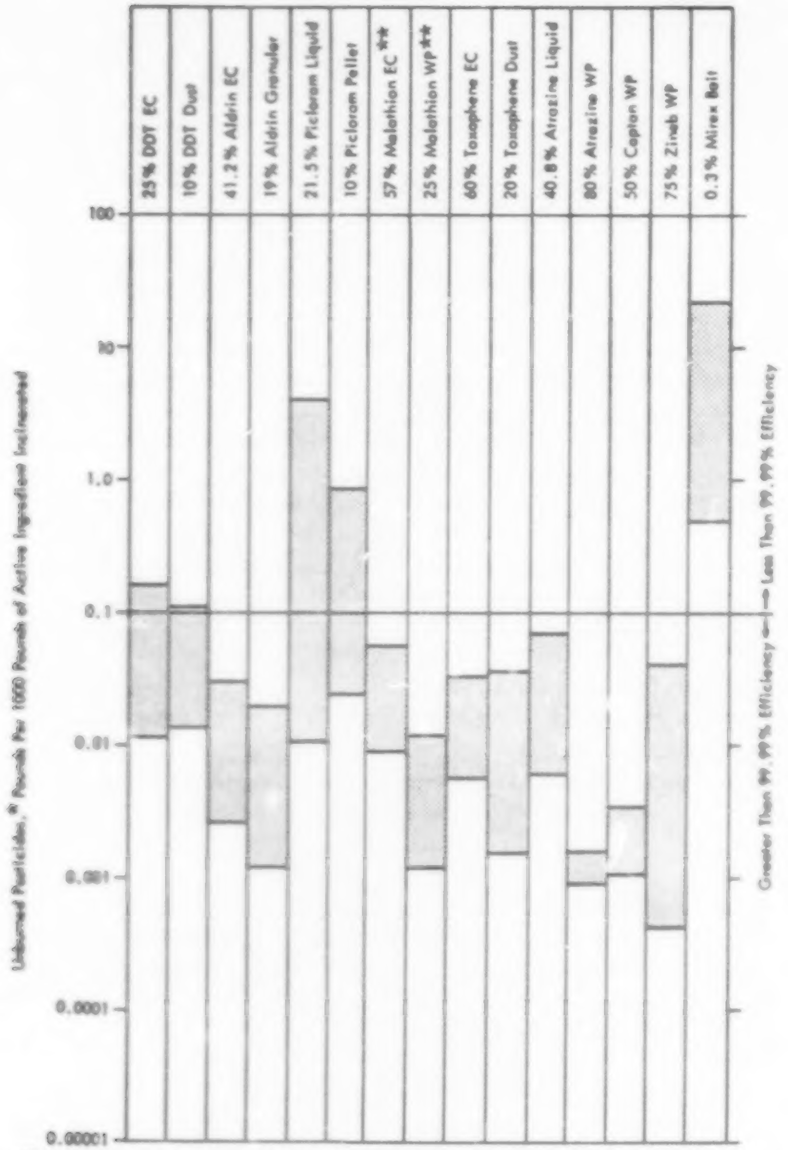
DISCUSSION

The results of this study show that the organic pesticides in 14 of the 15 formulations tested were effectively incinerated, i.e., > 99.99% degradation, over a range of time-temperature conditions. Of the 137 experiments conducted at primary-chamber retention times and temperatures ranging from 1.5 sec at 1200°C to 7 sec at 600°C, only 23 tests had an efficiency of < 99.99%. Ten of these 23 were tests using the 0.3% mirex bait formulation, and only six of the remaining 13 tests were conducted within a normal range of excess air (50 to 150%).

The total species output ratios $\left[\frac{\text{Quantity out}}{\text{Quantity in}}\right]$ as discussed on page 35), were used to evaluate incinerator performance at various operating conditions. These output ratios were the total amount of pesticide plus all related chemical species detected (total species) in the off-gas and solid residues per unit weight of active ingredient incinerated. The ranges of total species output ratios for all 15 formulations (137 tests) expressed as pounds total species in the off-gas and solid residues per 1,000 lb of active ingredient incinerated, are given in Figure 7.

The output ratios were tabulated in a matrix with the key incinerator operating variables--chamber temperature, flame temperature, retention time, percent excess air, fuel/feed ratio and off-gas rate. As expected, data comparisons showed that the operating variables were interrelated and could not be evaluated separately.

The matrix for each series of pesticide tests was then analyzed to determine the combinations and limits of the operating variables which yielded the lowest and highest values for the output ratios, i.e., best and worst conditions. This method of analysis showed the two most critical operating variables to be the retention time and primary chamber temperature. The excess air was not as critical but best results occurred at about 120%, with a range from 80 to 160%.



* The respective pesticide plus all related chemical species detected in the incinerator off-gas and solid residues.

** The range for malathion off-gas emissions is based on its detection limit.

Figure 7. Ranges or total species output ratios for the 15 formulations tests

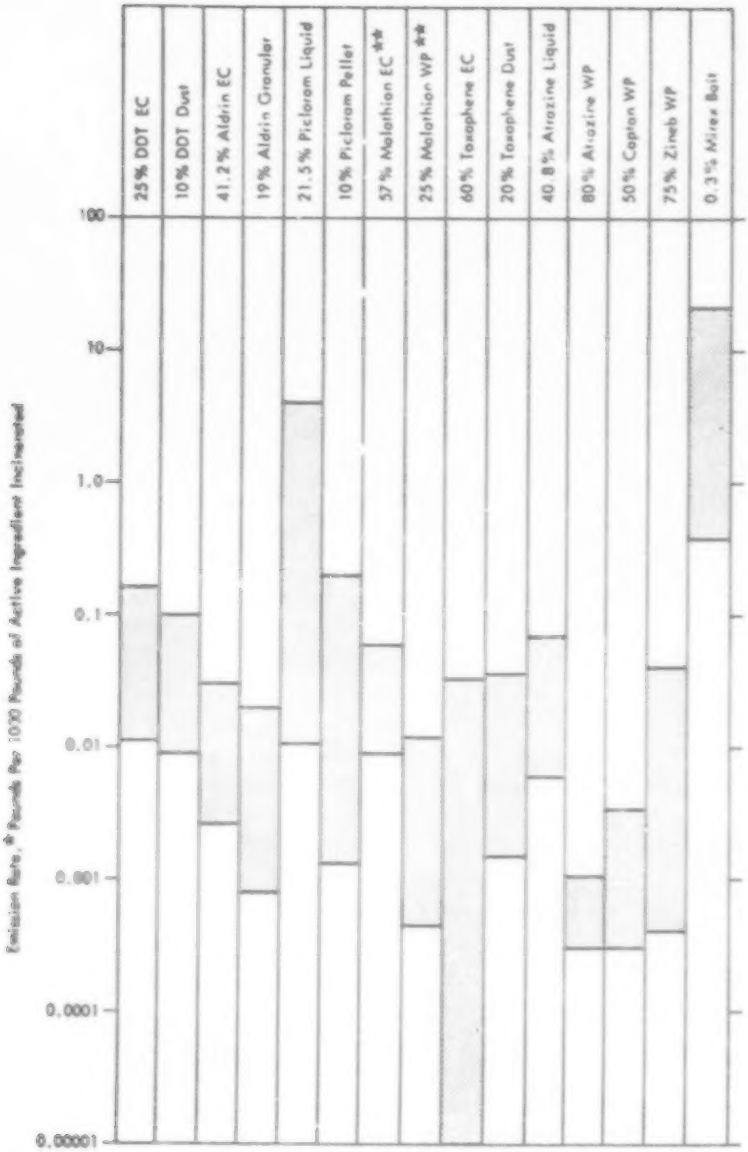
An evaluation was then made of the characteristics of the off-gas from the pesticide incineration tests. The ranges of total species emissions in the incinerator off-gas, expressed as pounds of total species in the off-gas per 1,000 lb of active ingredients incinerated, are shown in Figure 8.

The results of tests conducted for each pesticide in proximity to primary chamber time-temperatures of 2 sec at 1000°C were compared. (The 0.3% mirex formulation was excluded from this analysis because of the limited data in the time-temperature area of interest.) Interpolation of these data was used to estimate the total species emissions in the off-gas when incinerating at 2-sec retention at 1000°C and within the excess air range of 80 to 160%. These estimates, expressed as pounds of total species in the off-gas per 1,000 lb of active ingredients incinerated, are given in Figure 9.

An evaluation was made of comparable results for all 15 formulations tested in an attempt to hypothesize operating conditions (retention time and temperature) applicable to organic pesticides in general. Reference to Figure 7 shows that the point of greatest commonality in output ratios is 0.01, which corresponds to an incineration efficiency of one order of magnitude "better" than 99.99%. Output ratios for all tests having a nominal value of 0.01 were plotted as shown in Figure 10a. Data points in Figure 10a representing essentially the same value for a given pesticide formulation have been connected; these multiple points indicate the magnitude of the range over which essentially the same results have been obtained.

Figure 10b has been based on the data in Figure 10a and shows three areas of incinerator operations: Zone A represents operating conditions at which < 99.99% efficiency may result; the Operating Zone represents conditions at which efficiencies of at least 99.99% are expected; and Zone B represents conditions at which efficiencies of > 99.99% are anticipated. Thus, the acceptable operating zones from Figure 10b, in combination with lower temperature limits determined from DTA and TGA, can be used to estimate necessary operating conditions for the incineration of a given organic pesticide.

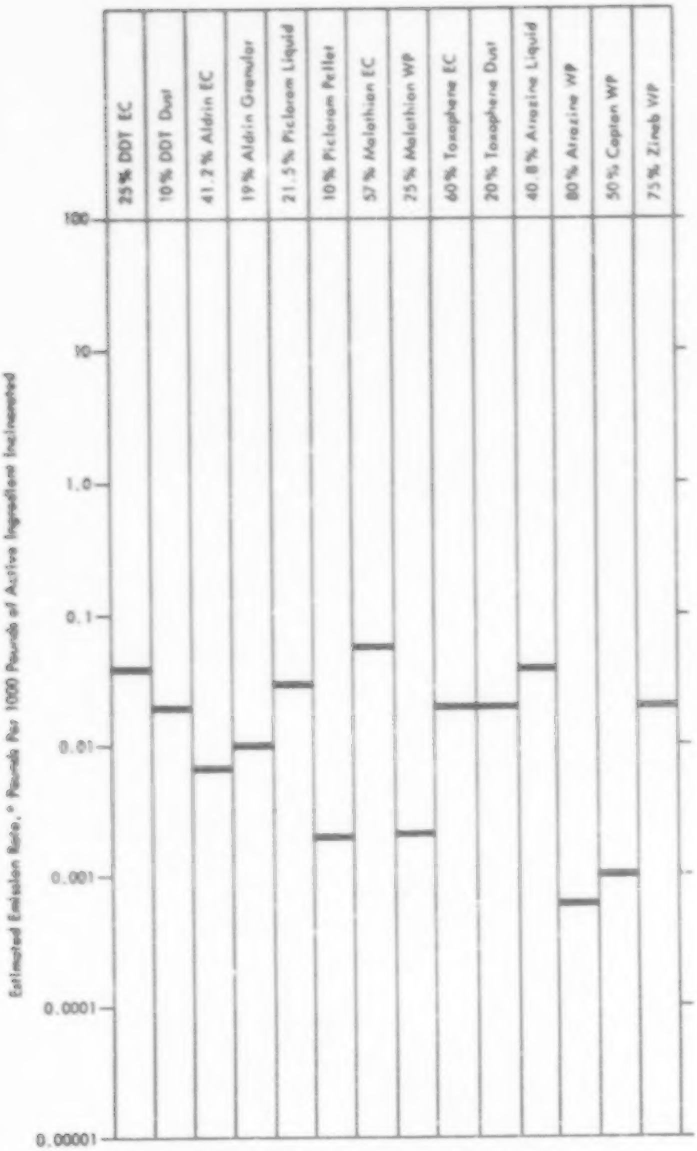
The preceding analysis of incineration efficiency has considered only the unburned and partially decomposed pesticide in the effluents. Additional factors that must be considered include the other potential off-gas pollutants generated, such as particulates, cyanide, pyrophosphates, sulfur dioxide, and oxides of nitrogen. Particulate emissions, as shown in Section V, exceeded the federal new source standard of 183 mg/m^3 for all of the solid formulations tested. (The 0.3% mirex formulation on a combustible corncob-grit base met the standard for four of 10 tests.)



* The respective pesticide plus all related chemical species detected in the incinerator off-gas.

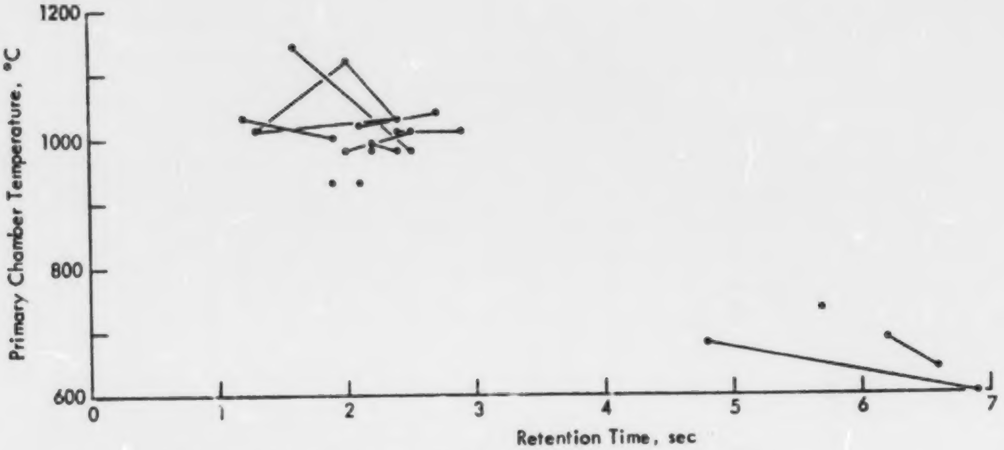
** The range for malathion is based on its detection limits.

Figure 8. Ranges of total species off-gas emissions for 15 formulations tests

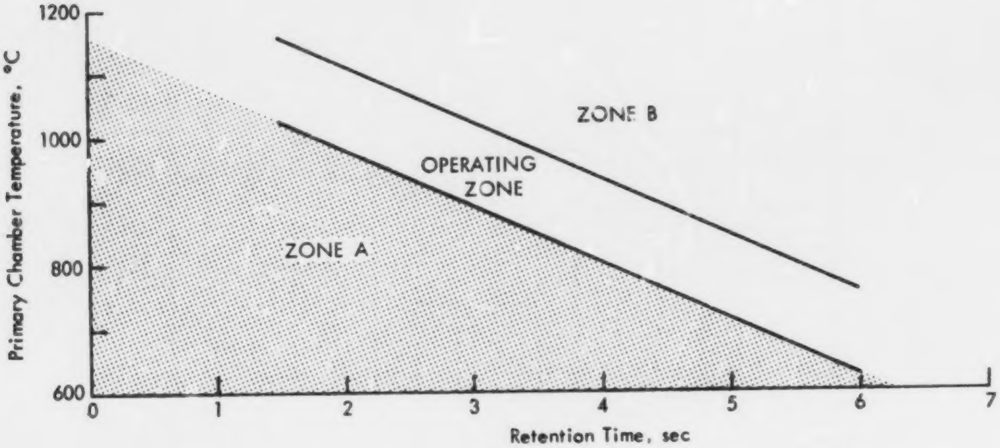


* The respective pesticide plus all related chemical species in the incinerator off gas.

Figure 9. Estimated total species off-gas emission rates at 2 sec retention time and 1000°C



a. Output ratios of ~ 0.01 for all pesticides tested.



b. Operating zones for pesticide incineration at 80 to 160% excess air.

Figure 10. Time-temperature zones for pesticide incineration.

As might be expected, the off-gas measurements for incineration of the nitrogen-containing pesticides (atrazine, captan, picloram, and zineb) indicated some cyanide (CN^-). The amount of cyanide generated was to some extent a function of chamber temperature and excess air and can apparently be minimized at the higher temperatures (1000°C or above with 120% excess air). Pesticides containing sulfur (captan, zineb, and malathion) also generate high levels of SO_2 in the off-gas (up to 8,000 mg/m^3 for the 57% malathion emulsifiable concentrate and 22,900 mg/m^3 for 75% zineb wettable powder). Malathion also showed to 3 g/hr of pyrophosphates in the off-gas. All of these off-gas products indicate the need for adequate particulate removal and scrubbing devices in the exhaust systems of pesticide incinerators.

SIGNIFICANCE OF TEST RESULTS

The test results and evaluated data have led to the hypothesized primary chamber temperature-retention time curves and operating zones shown in Figure 10b. These curves are related to the pesticides tested, the incinerator type and size, and the method of pesticide injection. Although the active ingredients and formulations tested represent a broad spectrum, the curves can only be recommended as a guideline for the incineration of other pesticides. The incinerator type and size do not appear to present major design problems, as long as sufficient retention time, mixing, and chamber temperature are maintained. However, the method of injection is significant, especially for the liquid formulation mixed with fuel oil prior to injection into the incinerator. (Here the flame temperature was "seen" by all of the liquid pesticides and, as a result, the primary chamber temperature may not be a good indication of the required temperature.) Thus, testing of grate-type incinerators with typical containers of liquid and solid pesticide formulation is needed before attempting to burn bulk pesticides, i.e., packages, jugs, etc., in these incinerators. The results from this research study cannot be extrapolated to the incineration of bulk pesticides or pesticide-containing solid waste without additional testing. An oil burner or auxiliary injection nozzle may be used in grate-type incinerators to spray the pesticide into the chamber with the chamber operated at conditions to meet time, temperature, and air requirements.

PESTICIDE INCINERATION SYSTEM DESIGN ANALYSIS

Incinerator

The retention time, chamber temperature, and excess air limits for good incineration of the pesticide formulations tested during this program have been indicated in Figure 10b. Based on these results, it appears that any type of incinerator capable of meeting the retention time and primary combustion chamber temperature requirements with 80 to 160% excess air is a potential candidate for use in incineration of pesticides. However, these guidelines have been developed from the results of tests in which all pesticides were injected into the primary chamber through nozzles; no tests were run with bulk containers of liquids or powders. Because of this limitation, only incinerators having similar provisions for injection of the pesticides can be used. An alternative is to modify existing incinerators by adding a suitable pesticide injection nozzle into the primary chamber. The incineration of bulk amounts of pesticides on grates cannot be recommended without further tests.

Pesticide incinerators should be classified as a Class VII,* incinerators requiring special design for the waste to be incinerated. However, the Class IA (small) and Class V (municipal) incinerators should be useable with appropriate feed nozzle additions since both classes appear to include adequate retention time, temperature, and excess air.

Design information for pesticide incineration are included in Table 18. The capacity, heat release rate, and flue gas volume rate values (on a unit primary chamber volume basis) are directly useable to calculate the potential capacity, heat release rate, and flue gas volume rate for use in design or for evaluating the capacity of an existing incinerator. The fuel/pesticide ratio is also presented and can be useful as a guide for supplemental fuel requirements to maintain adequate temperatures.

Additional considerations in the design of incinerators for pesticides include mechanical design, instrumentation, materials handling and safety. Proper materials of construction will be needed to prevent corrosion, and the design must consider the affect of thermal cycling if the facility is to be operated on an intermittent basis. At least minimum instrumentation must be provided to routinely determine primary combustion chamber temperature and percent excess air. Adequate provision for storage and handling of the pesticide and for the safety of the operating personnel must also be included.

Air Pollution Control Considerations

The results of the incinerator off-gas sampling and analyses identified several types of emissions which must be considered in the design and operation of a pesticide incineration system. Particulates and various gaseous pollutants in significant concentrations were measured at levels which exceeded appropriate federal new source performance standards.

---

* Incinerator classification of the Incinerator Institute of America.19/

Table 18. DESIGN DATA FOR PESTICIDE INCINERATION

	Pesticide formulation properties			Incinerator information			
Pesticide	Composition	Density kg/m³ (lb/cu ft)	Heat of combustion J/kg (Btu/lb)	Capacity[a] ℓ/hr/m³ (gal/hr/cf)	Heat release[a] rate J/hr/m³ (Btu/hr/cf)	Flue gas[b] volume rate m³/m/m³ dscfm/cf	Fuel/Pesticide ratio (ℓ/ℓ) or (gal/gal)
Liquid formulations							
DDT	25% EC	958 (59.8)	3.47×10^7 (14,920)	28 (0.21)	9.3×10^8 (25,100)	15.2	0-1.6
Aldrin	41.2% EC	1,102 (68.8)	3.10×10^7 (13,330)	11 (0.08)	3.6×10^8 (9,800)	10.4	0.5-1.8
Picloram	21.5% water-base	958 (59.8)	7.82×10^6 (3,360)	19 (0.14)	1.4×10^8 (3,800)	10.0	0.7-0.9
Malathion	57% EC	1,126 (70.3)	2.79×10^7 (12,020)	9 (0.07)	2.9×10^8 (7,900)	3.5	0
Toxaphene	60% EC	1,198 (74.8)	2.58×10^7 (11,190)	8 (0.06)	2.5×10^8 (6,700)	2.6	0.5-0.7
Atrazine	40.8% flowable	1,115 (69.6)	2.47×10^7 (10,630)	23 (0.17)	6.3×10^8 (16,800)	4.7	0.3
Solid formulations							
				kg/hr/m³ (lb/hr/cf)			ℓ/kg (gal/kg)
DDT	10% dust	-	-	52.4 (3.27)	-	9.7	0.26 (0.031)
Aldrin	19% granules	-	5.71×10^6 (2,460)	27.7 (1.73)	1.6×10^8 (4,250)	8.7	0.47 (0.055)
Picloram	10% pellets	-	1.12×10^6 (480)	43.9 (2.74)	4.9×10^7 (1,320)	6.5	0.28 (0.034)
Malathion	20% dust	-	5.51×10^6 (2,370)	26.6 (1.66)	1.5×10^8 (3,940)	4.2	0.44 (0.052)
Toxaphene	20% dust	-	3.29×10^6 (1,410)	25.5 (1.59)	8.4×10^7 (2,250)	9.6	1.70 (0.202)
Atrazine	80% WP	-	2.02×10^7 (8,690)	6.4 (0.40)	1.3×10^8 (3,480)	8.0	0.54 (0.064)
Captan	50% WP	-	9.17×10^6 (3,940)	9.0 (0.56)	8.2×10^7 (2,210)	9.2	1.01 (0.120)
Zineb	75% WP	-	1.29×10^7 (5,550)	6.6 (0.41)	8.4×10^7 (2,250)	7.8	1.60 (0.191)
Mirex	0.3% bait on corncob grit	-	2.17×10^7 (9,330)	32.0 (2.00)	6.9×10^8 (18,600)	10.0	0.25 (0.030)

---

[a] Maximum capacity during tests with incineration efficiencies of 99.99% or greater incineration. Values divided by primary test chamber volume 0.725 m³ (25.6 cu ft).

[b] Based on maximum measured flow corrected to standard conditions of one atmosphere pressure and 21.1°C (70°F) and divided by the primary chamber volume, 0.725 m³ (25.6 cu ft).

Specific pollutants of concern for a given pesticide or generic group of pesticides included the following:

1. Nitrogen-containing pesticides can emit significant concentrations of cyanide (CN^-) (captan, 49 mg/m^3; zineb, 138 mg/m^3).

2. Phosphorus-containing pesticides emit P_2O_5.

3. Sulfur-containing pesticides may emit sulfur dioxide (levels as high as 8,000 mg/m^3 from malathion and 22,900 mg/m^3 for zineb).

4. Solid formulations (powders, dusts, granules, pellets) can emit large quantities of particulates depending on the type and size of carrier medium (up to 71,000 mg/m^3 for DDT; 73,000 mg/m^3 for toxaphene).

5. Incineration of certain pesticides results in emission of other gaseous pollutants such as HCl, Cl_2, CO, NO_x, etc.

The emission levels of the above pollutants for any incinerator will be a function of the pesticide fed, feed rate, excess air, combustion chamber temperature, and retention time. However, the fact that significant emission levels were recorded during the course of this work indicates the need of providing stack gas cleanup equipment to remove potentially harmful gases and to meet incinerator effluent standards.

The design of an air pollution abatement system for a pesticide incinerator will be highly dependent on the specific purposes for which the incinerator will be used, i.e., type and formulations fed. There is insufficient information from this work to delineate specific control equipment design data, but some generalized design considerations can be suggested.

Applications with high particulate concentrations in the effluent (as have been measured for most of the solid formulation tests) will probably require equipment with high mass and fractional collection efficiencies. Depending on the moisture content of the flue gas stream and flue gas temperature, potential control devices include cyclones, fabric filters or electrostatic precipitators.

If a cyclone collector is used, it would probably be included as a precollector, followed by a collector with better efficiency potential. As an extreme example of the possible collection efficiency required, the maximum particulate loading measured was 73,000 mg/m^3 for 20% toxaphene dust. In order to meet a particulate effluent standard of 183 mg/m^3, the mass efficiency of the control system would need to be in excess of 99.75%. Depending on the particle size distribution of the particulate (which was not determined), a cyclone collector may have difficulty achieving this level of collection. Fabric filters and electrostatic precipitators are much more efficient; however, they are both sensitive to gas conditions, gas composition and other particulate properties (resistivity, chemical composition, etc.).

The collection equipment of choice for the gaseous pollutants would be a wet scrubber. There are a wide variety of possible scrubber types which might be used. Table 19 is a listing of scrubber systems which have been applied to combustion processes and for removal of gaseous pollutants.[24] Some of these systems may prove to be adequate for particulate collection as well.

Table 19. SCRUBBER TYPES AND APPLICATIONS

Scrubber type	Application[a]
Plate	P, G
Packed tower	G
Fiber bed	G
Spray tower	G
Venturi	P
Centrifugal	P
Moving bed	P, G

---

[a] P = Particulate removal
G = Gaseous pollutant removal

The particular gaseous pollutant of interest may require scrubbing with a medium specific for the pollutant. Water is adequate for a gas such as HCl, but other scrubber media may be required for SO_2, NO_x, etc. In some cases, multiple stages will be required to efficiently remove a combination of gaseous pollutants, with each stage specific for a given pollutant.

Several other design considerations are worthy of note. Proper materials of construction will be necessary to prevent corrosion of duct work, scrubber vessels, pumps, piping and nozzles. Proper design techniques for duct velocities will be necessary to prevent settling of particulate in horizontal duct runs. Scrubber wastewater and associated sludge may require further treatment before disposal. Each facility may have unique characteristics which must be considered in the light of appropriate federal, state, and local effluent standards and must be designed to operate within these constraints.

Research Needs

The results of this study, as have been discussed in the preceding sections, point to areas requiring additional investigation. (A detailed list of these needs has been presented in Section II - Recommendations.)

These needs can be categorized into three major areas.

First, more work is needed at the pilot scale in order to determine necessary combustion conditions for (a) additional pesticides representative of other chemical subclasses, and (b) pesticide containing solid wastes.

Second, the generalized incinerator operation and design guidelines developed by this study should be verified or revised utilizing the additional data. The guidelines must then be confirmed by a limited number of full-scale tests.

Third, sufficient additional research must be done on the characteristics of effluents from pesticide incineration to specify adequate emission control devices.

SECTION VII

REFERENCES

1. Working Group on Pesticides, "Proceedings of the National Working Conference on Pesticide Disposal," at the National Agricultural Library, Beltsville, Maryland, 30 June and 1 July 1970, NTIS No. PB 197 145 (September 1970).

2. Federal Working Group on Pest Management, "Proceedings of the National Conference on Pesticide Containers," New Orleans, Louisiana, 28-30 November 1972 (December 1972).

3. Working Group on Pesticides, "Summary of Interim Guidelines for Disposal of Surplus or Waste Pesticides and Pesticide Containers," NTIS No. AD 720 391 (December 1970).

4. Lawless, E. W., T. L. Ferguson, and A. F. Meiners, "Guidelines for the Disposal of Small Quantities of Unused Pesticides," (Draft Final Report), EPA Contract No. 68-01-0098 (August 1974).

5. 7 USC 135 et seq. The Federal Insecticide, Fungicide, and Rodenticide Act, Section 2, as amended Public Law 92-516, "Federal Environmental Pesticide Control Act of 1972" (21 October 1972).

6. Environmental Protection Agency, "Pesticides and Pesticide Containers: Regulations for Acceptance and Recommended Procedures for Disposal and Storage," *Federal Register*, **39**(85):15236-15241 (1 May 1974).

7. Environmental Protection Agency, "Pesticides and Pesticide Containers: Proposed Regulations for Prohibition of Certain Acts Regarding Disposal and Storage," *Federal Register*, **39**(200):36867-36870 (15 October 1974).

8. Hanneman, W. W., and R. S. Porter, "The Thermal Decomposition of Dialkyl Phosphates and O,O-Dialkyl Dithiophosphates," *J. Organic Chem.*, **29**:2996 (October 1964).

9. Anthony, W. S., and F. L. Shuman, Jr., "Disposal of Liquid Pesticides by Incineration," Paper No. 71-148, 1971 Annual Meeting American Society of Agricultural Engineers, Pullman, Washington (27-30 June 1971).

10. Putnam, R. C., F. Ellison, R. Protzmann, and J. Hilovsky, "Organic Pesticides and Pesticide Containers," Report No. EPA-SW-21C-71, Foster D. Snell, Inc., Florham Park, New Jersey (1971).

11. Whaley, H., G. K. Lee, R. K. Jeffery, and E. R. Mitchell, "Thermal Destruction of DDT in an Oil Carrier," Canadian Combustion Research Laboratory, Ottawa, Canada, Mines Br. Res. Rep., R225 (1970).

12. Lee, G. K., F. D. Friedrich, B. C. Post, and H. Whaley, "Thermal Destruction of DDT-Bearing Powders," Mines Br. Res. Rep., R234 (1971).

13. Kennedy, M. V., B. J. Stojanovic, and F. L. Shuman, Jr., "Chemical and Thermal Methods for Disposal of Pesticides, Res. Rev., **29**:89 (1969).

14. Stojanovic, B. J., M. V. Kennedy, and F. L. Shuman, Jr., "Edaphic Aspects of the Disposal of Unused Pesticides, Pesticide Wastes, and Pesticide Containers," J. Environ. Quality, **1**(1):54 (1972).

15. Kennedy, M. V., B. J. Stojanovic, and F. L. Shuman, Jr., "Chemical and Thermal Aspects of Pesticide Disposal," J. Environ. Quality, **1**(1):63 (January-March 1972).

16. Shuman, F. L., Jr., B. J. Stojanovic, and M. V. Kennedy, "Engineering Aspects of the Disposal of Unused Pesticides, Pesticide Wastes, and Pesticide Containers," J. Environ. Quality, **1**(1):66 (January-March 1972).

17. Kennedy, M. V., B. J. Stojanovic, and F. L. Shuman, Jr., "Analysis of Decomposition Products of Pesticides," J. Agr. Food Chem., **20**(2):341 (1972).

18. Stojanovic, B. J., F. Hutto, M. V. Kennedy, and F. L. Shuman, Jr., "Mild Thermal Degradation of Pesticides," J. Environ. Quality, **1**(4):397 (1972).

19. I.I.A. Incinerator Standards, Incinerator Institute of America, Inc., Arlington, Virginia (March 1970).

20. "Standards of Performance for New Stationary Sources," Federal Register, 36(247):24876-24895 (23 December 1971).

21. Carnes, R. A., EPA/NERC-SHWRL, Personal Communication to Mr. T. L. Ferguson (30 January 1974).

22. Herbicide Handbook of the Weed Science Society of America, 2nd ed., W. F. Humphrey Press, Inc., Geneva, New York (1970).

23. Capasso, N. S., L. Buckles, P. Cavey, F. Hildebrandt, and I. I. Stevens, U.S. Army Munitions Command, Edgewood Arsenal, Maryland, Personal Communication to Mr. T. L. Ferguson and Mr. Fred J. Bergman (14 September 1973).

24. Calvert, S., J. Goldshmid, D. Leith, and D. Mehta, "Scrubber Handbook," A.P.T., Inc., EPA Contract No. CPA-70-95 (July 1972).

APPENDIX A

EXPERIMENTAL EQUIPMENT

CONTENTS

Page

Incinerator. 90

Pesticide Injection System 92

  Liquid Pesticides. 92
  Solid Pesticides 99

Scrubber System. 99

Scrubber Water Treatment System. 107

Ancillary Equipment. 109

Preceding page blank

The experimental system was built at MRI's Deramus Field Station in Grandview, Missouri.

Facilities at the experimental site consisted of Laboratory Buildings Nos. 1 and 2. The incinerator was constructed adjacent to Building No. 1, which housed the scrubber and water treatment systems. Laboratory Building No. 2 provided storage and special laboratory facilities removed from the test area.

The overall system (Figure 1, p. 21) consisted of an incinerator (Figures 2, p. 22 and 11), a pesticide feed system (Figures 12 through 18), three scrubbers (Figure 1, p. 21) and a wastewater treatment system (Figure 19). Specific details on these components (in the actual system of units used for their design) follow under separate headings.

INCINERATOR

The experimental incinerator (Figures 2, p. 22 and 11) was constructed on a concrete pad adjacent to Laboratory Building No. 1.

The incinerator was constructed with an outer wall of concrete blocks and a liner of insulating firebrick. The void between the walls was filled with perlite insulation.

The incinerator was a two-chamber design separated by a checker wall. The primary chamber volume was approximately 25.6 ft^3 and the secondary chamber volume 20.6 ft^3. The design capacity was 100 lb/hr of Type I waste,* equivalent to 650,000 Btu/hr.

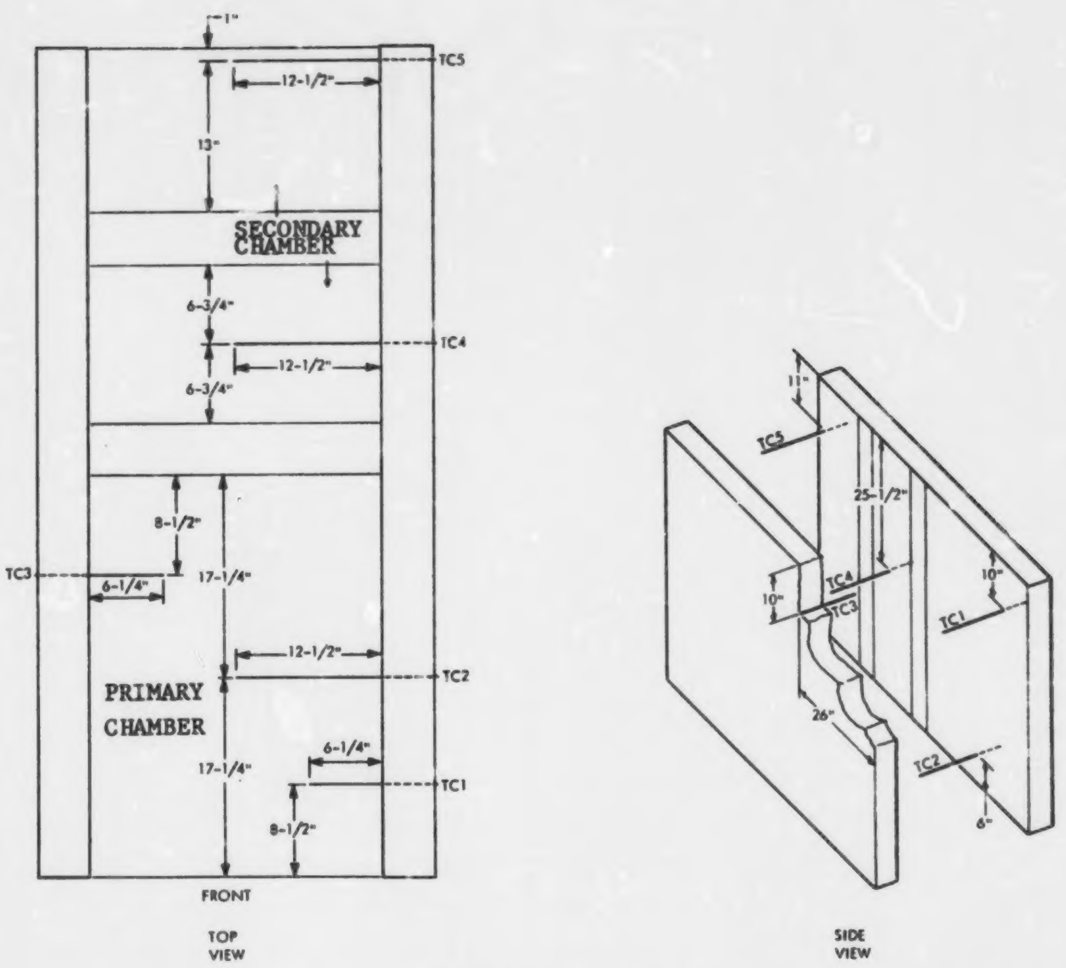
The primary chamber was constructed with two burner positions, one in front and an alternate on the side. Also in the front wall were a view port and near the bottom a sample port for collecting a grab sample of solid pesticides during incineration. Another port was located in the top of the primary chamber to facilitate pyrometer readings. The underfire air opening was located beneath the front burner opening.

A door was provided near the rear of the second chamber for cleaning out solid residues.

Five thermocouples (Figure 11) were installed in the incinerator, three in the primary chamber and two in the secondary chamber. Manometer

---

* I.I.A. Incinerator Standards, Incinerator Institute of America, Arlington, Virginia (March 1970).



INCINERATOR THERMOCOUPLE LOCATIONS

Figure 11. Incinerator thermocouple locations

connections for determining the differential pressure of the chamber during incineration were located adjacent to the front wall of each chamber (see Figure 5, p. 27).

Transition from the incinerator to the vertical stack was made by a square stack constructed from 1/8 in. sheet metal. Two openings were located in the square stack, one in the side near the front and one in the rear. These openings provided entrance for inspection cleaning.

The incinerator was covered with a roof serving as a partial protection from the weather and as a platform for particulate sampling.

The original design of the incinerator was made according to IIA standards for 100 lb/hr of Type I waste. Requirements and values for the design are given in Table 20. The elimination of the grating from the primary chamber resulted in the effective volume of the primary chamber being changed to 25.6 ft^3.

During the experimental tests the incinerator operated under induced draft provided by a blower (Figure 1, p. 21). During warm-up periods when only fuel oil was being burned, the incinerator was operated by natural draft by opening the stack bypass and venting to the atmosphere.

PESTICIDE INJECTION SYSTEMS

Liquid Pesticides

For liquid formulations, two types of injection systems were used, one for fuel oil miscible liquids and the second for water-based pesticides.

The injection method used with fuel oil miscible liquid pesticides (Figure 12) was to mix the pesticide with fuel oil feeding the burner (Figures 13 and 14).

For water based liquid pesticides, a separate system was used which consisted of a pump and a fuel oil burner nozzle (Figure 15). The pesticide nozzle and the fuel oil burner were located on a horizontal plane and at a 30 degree angle to each other in the primary burner position (see Figure 2, p. 22). The pesticide was passed through a water-cooled jacket and then through a conventional fuel oil nozzle (Figure 16). The water-cooled jacket prevented the pesticide injection system from plugging when exposed to the heat of the incinerator.

Table 20. INCINERATOR DESIGN PARAMETERS[a]

Basic Ratio: 100 lb/hr of Type I waste = 650,000 Btu/hr maximum
Stack velocity = 165 ft/min
= 18 ft^3/sec at 1400°F
Settling chamber velocity = 9 ft/sec
Cross-section in secondary chamber = 1.56 ft^2
Grate area equivalent = 5.25 ft^2
Primary chamber = 20 ft^3
Secondary chamber = 24 ft^3
Surface area = 71 ft^2
Radiation rate = 9,155 Btu/ft^2/hr
Stack = 12 in. diameter
No. 2 fuel oil at 18,900 Btu/lb
= 110,000 Btu/gal
Air required at 100% excess
7.0 lb/10,000 Btu = 455 lb/hr

---

[a] Based on I.I.A. Incinerator Standards, Incinerator Institute of America, Arlington, Virginia (March 1970).

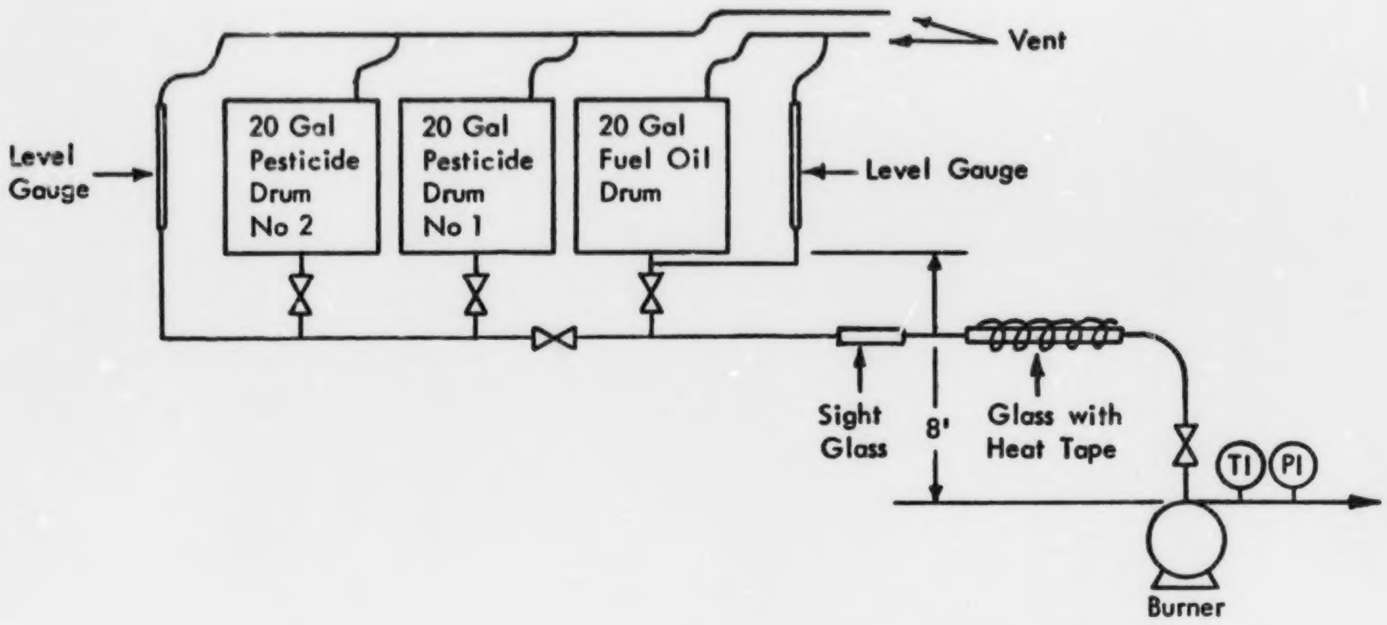
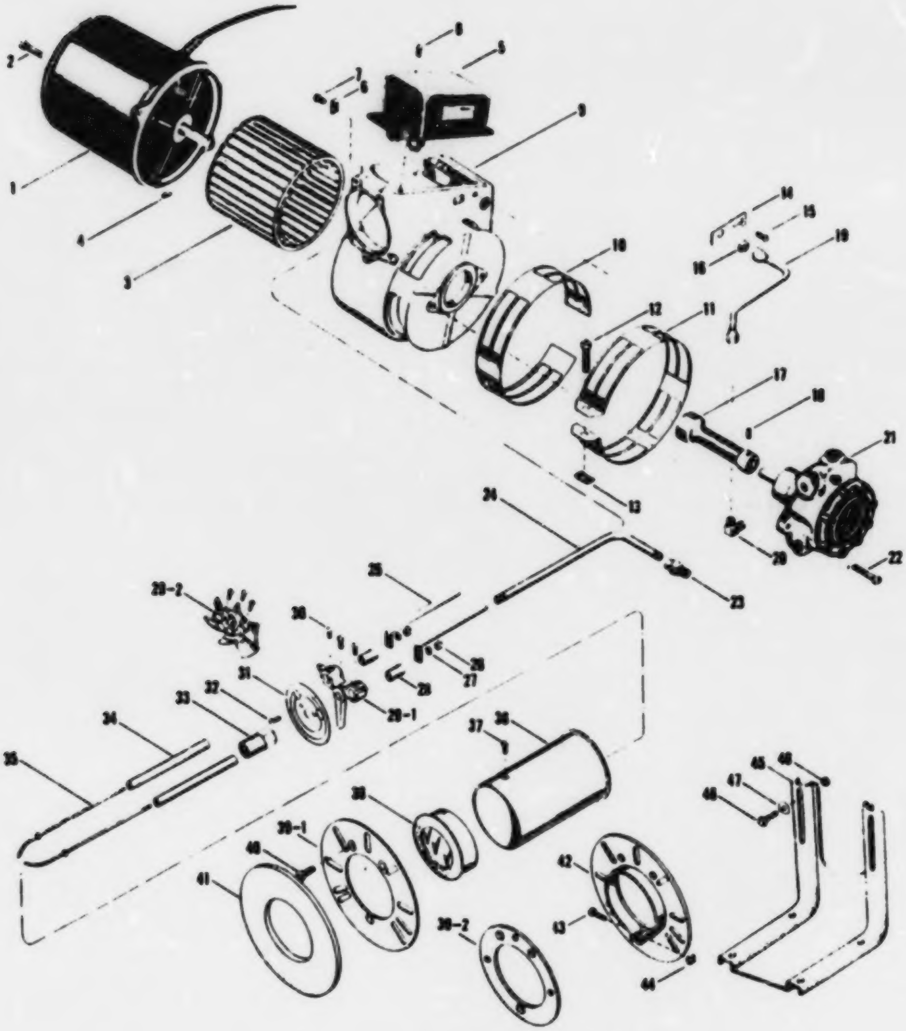


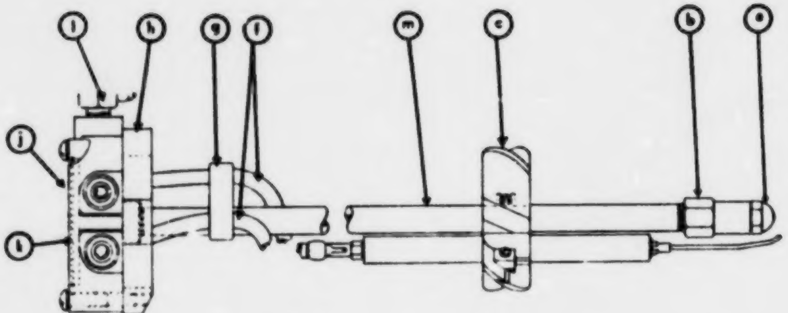
Figure 12. Liquid pesticide feed system - fuel oil miscible formulations



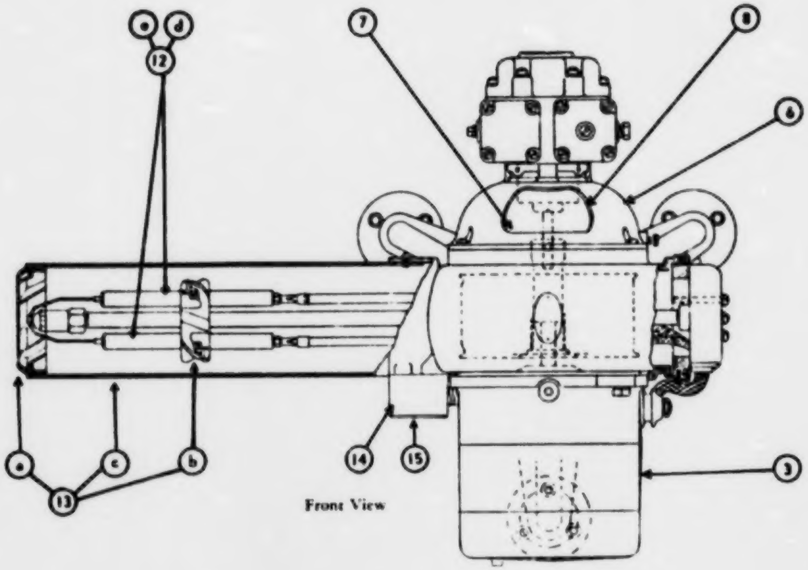
PARTS LIST

ITEM NO.	DESCRIPTION	ITEM NO.	DESCRIPTION	ITEM NO.	DESCRIPTION
1	Motor, 1/8 HP	17	Pump Coupling	33	Nozzle Adapter
2	Motor Mt'g. Fil. Hd. Mach. Screw	18	Pump Coupling Set Screw	34	Insulator
3	Fan	19	Oil Line Assembly	35	Electrode Stem and Washer
4	Fan Set Screw	20	Oil Line Elbow	36	Air Tube
5	Transformer	21	Fuel Unit	37	Air Cone Mt'g. Fil. Hd. Mach. Screw
6	Hinge Clip	22	Fuel Unit Mt'g. Fil. Hd. Mach. Screw	38	Air Cone
7	Self Tapping Screw	23	Oil Line Fitting	39-1	Large Flange - 9 in. O. D.
8	Rd. Hd. Screw	24	Oil Pipe	39-2	Small Flange - 6-1/4 in. O. D.
9	Fan Housing	25	Buss Bar	40	Flange Mt'g. Fil. Hd. Mach. Screw
10	Air Adj. Band - Inner	26	Hex Nut	41	Gasket
11	Air Adj. Band - Outer	27	Washer	42	Adj. Flange
12	Air Band Fil. Hd. Mach. Screw	28	Insulator Bushing	43	Fil. Hd. Mech. Screw
13	Tinnerman Speed Nut	29-1	Electrode Support	44	Square Nut
14	Oil Line Adj. Slot Cover	29-2	Stabilizer	45	Support Bracket
15	Oil Line Slot Cover Screw	30	Rd. Hd. Mech. Screw	46	Hex Hd. Mech. Screw
16	Oil Line Lockout	31	Baffle Plate	47	Washer
		32	Rd. Hd. Mach. Screw	48	Hex Nut

Figure 13. Diagram of 0.6 to 3.0 gal/hr fuel oil burner.



(12) TAILPIECE ASSEMBLY



Front View

ITEM NO.	NAME OF PART OR ASSEMBLY
1.	Blower Case
2.	Pedestal Assembly
	a. Pedestal Column
	b. Hex Jam Nut
	c. Pedestal
3.	Motor. G. E. ⅓ H.P.. Type E.H.
4.	Fan—Torrington 37 Blade —Type No. 1. 45 Blade
5.	Fuel Pump. Webster
6.	Air Shutter Housing
7.	Air Shutter
8.	Air Shutter Retaining Spring
9.	Thumb Screw
10.	Flexible Coupling
11.	Transformer (Give voltage. cycles). Gardner
12.	Tail Piece Assembly
	a. Nozzle Tip (Specify capacity. angulation)
	b. Nozzle Adapter
	c. Air Deflector & Electrode Holder
	d. Electrode (Right)
	e. Electrode (Left)
	f. Ignition Cable
	g. Ignition Cable Spacer
	h. Tailpiece Collar
	i. Tailpiece
	j. Tailpiece Glass Retainer
	k. Tailpiece Glass
	l. Imperial Elbow Fitting
	m. Fuel Tube
13.	Blower Tube Assembly
	a. Air Diffuser
	b. Tailpiece Support
	c. Blower Tube
	d. Air Diffuser Adjustment Rod (not shown)
	e. Wing Nut (not shown)
14.	Junction Box
15.	Junction Box Cover
16.	Fuel Feed Pipe Assembly
17.	BX Conduit
18.	BX Connector
19	Anti Short
20.	Burner Bracket Mounting Assembly
	a. Burner Mounting Stud
	b. Burner Mounting Rod
	c. Burner Mounting Washer (1)
	d. Burner Mounting Washer
	e. Rubber Mounting
21.	Burner Bracket Assembly

Figure 14. Diagram of 3.0 to 8.0 gal/hr fuel oil burner

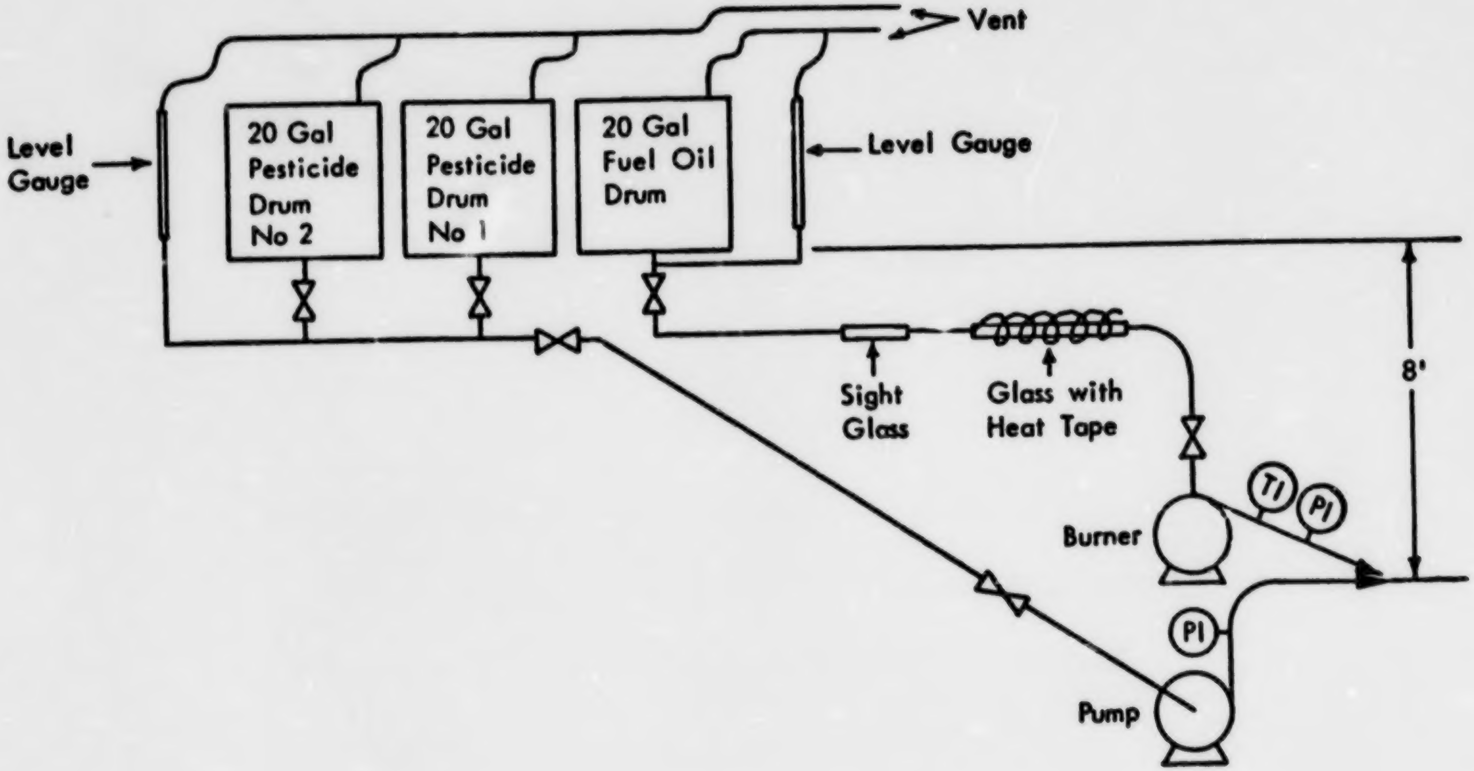
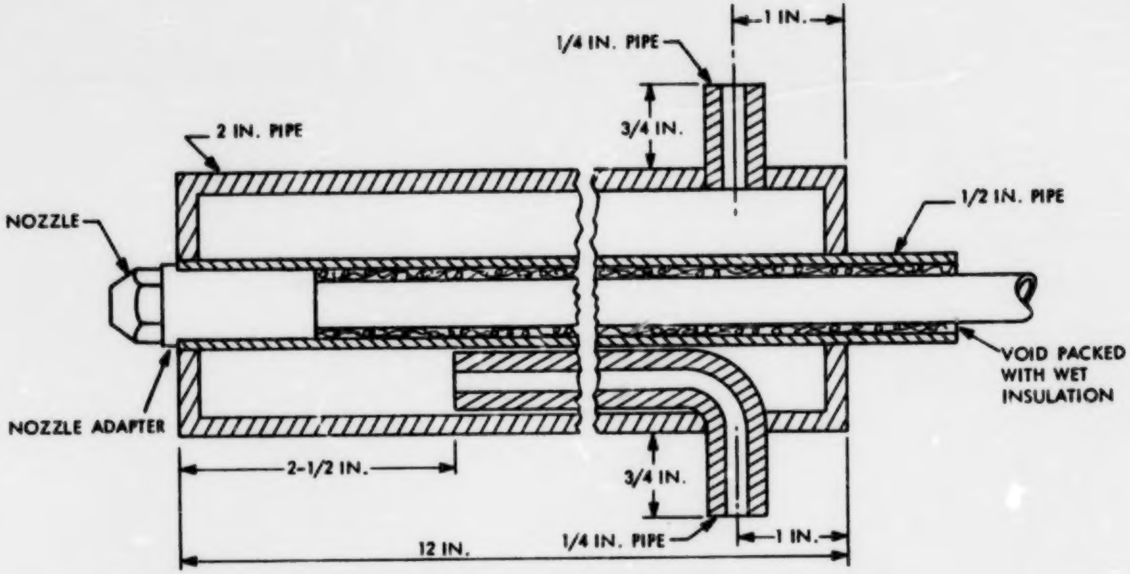
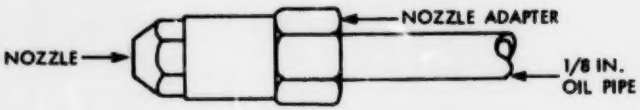


Figure 15. Liquid pesticide feed system-water based formulations



B. MODIFIED, WATERCOOLED INJECTION NOZZLE



A. STANDARD BURNER NOZZLE

Figure 16. Modified injection nozzle

Both liquid pesticide injection systems were fed from drums situated on a platform inside Laboratory Building No. 1. The platform was 8 ft above the center line of injection. The feed drums were vented outside the building.

The feed line to the burner was equipped with an electrical heat tape for use during cold weather. (Heating of the water-based pesticide feed line was unnecessary because all of the water based liquid pesticides were incinerated during the summer months.)

Pressure gauges were installed on both the fuel oil burner and the water base pesticide pumps. The burner also had an oil temperature indicator.

The feed drums for both the fuel oil and pesticide mixture had level gauges for use in determining the flow rate.

Solid Pesticides

The solid pesticide injection system is shown in Figure 17. The pesticide was fed into a flexible hose from a vibrating screw feeder. Compressed air was injected into the feed line, forcing the pesticide through a water cooled injection nozzle (Figure 18).

The fuel oil burner and the water cooled injection nozzle were located in the primary burner position and on a horizontal plane and at a 30 degree angle to one another.

The vibrating screw feeder was equipped with a variable speed drive allowing the delivery rate to be changed. This feature also adapted well to the different active ingredient contents and particle sizes of the various solid pesticide formulations.

The compressed air passed through two water traps before entering the injection system to prevent plugging problems with dust formulations.

SCRUBBER SYSTEM

The purpose for installing a scrubber system was to prevent potential emissions of pesticides into the environment.

The experimental scrubber system (see Figure 1, p. 21) consisted of three separate scrubbers; the first and third used water as the scrubbing liquid and the second, hexylene glycol. Design criteria for the scrubber system appear in Table 21.

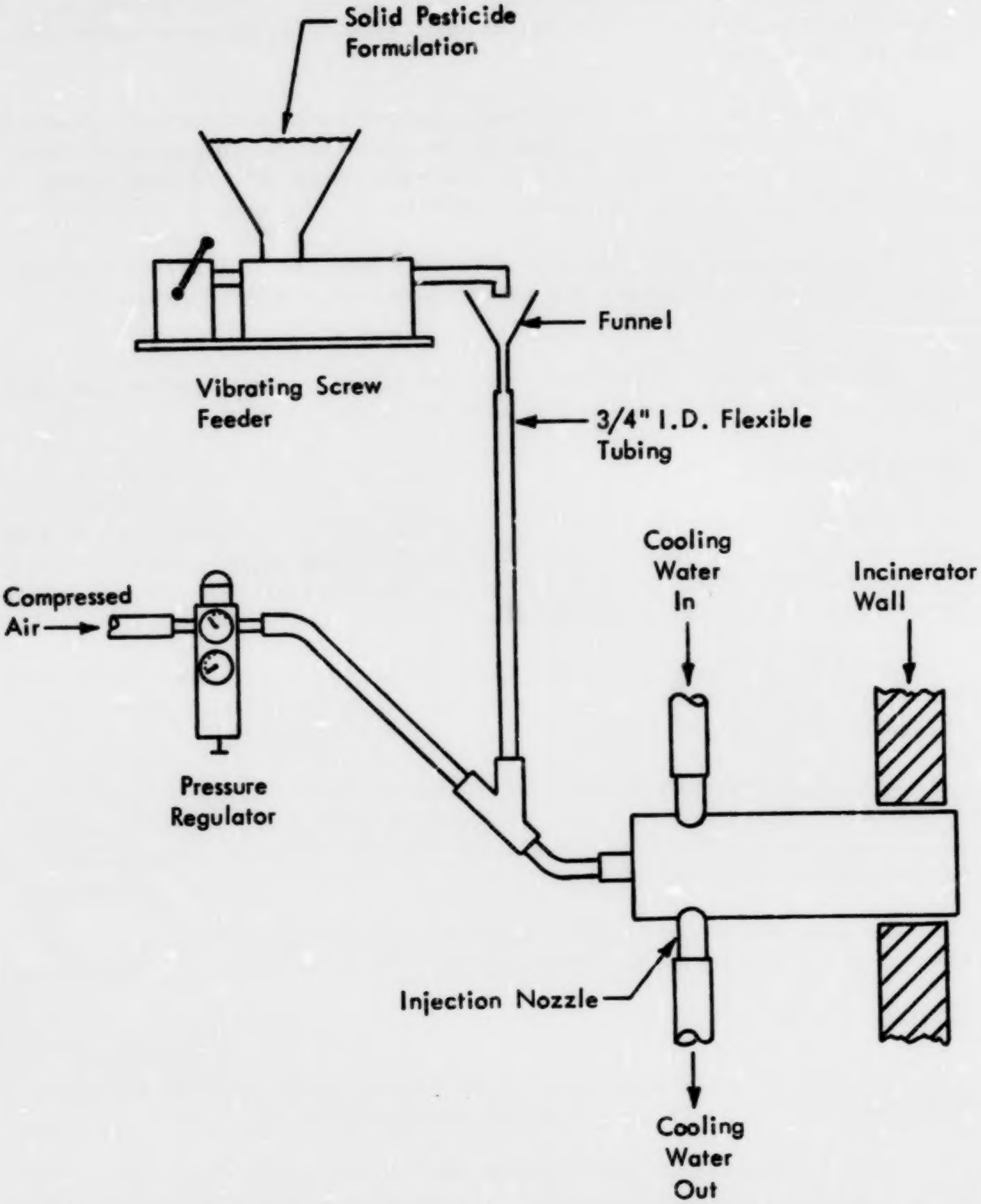


Figure 17. Solid formulation injection system

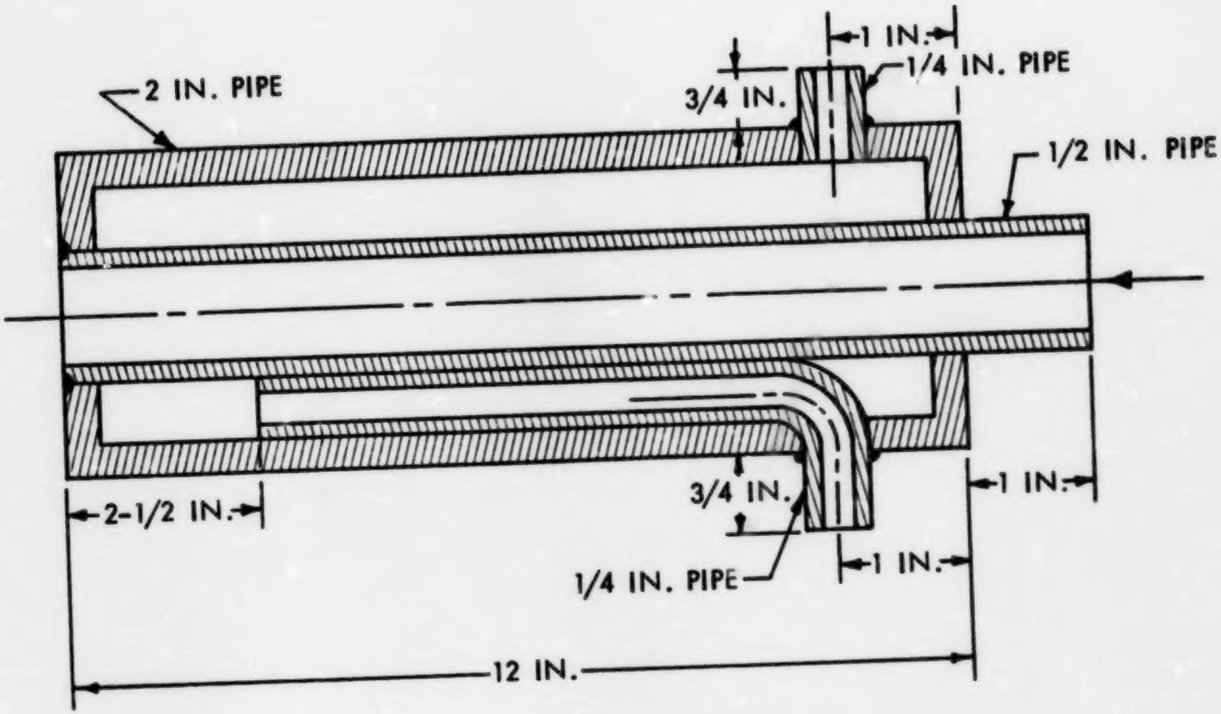


Figure 18. Dust injection nozzle

Table 21. DESIGN OF SCRUBBING SYSTEM

1. Scrubber No. 1

Calculate cross-sectional area of the marble bed

Use superficial velocity of 500 ft/min

Gas flow is ≈ 300 acfm

$$\frac{300 \text{ acf/min}}{500 \text{ ft/min}} = 0.60 \text{ ft}^2$$

$$\text{Area} = \frac{\pi}{4} d^2$$

$$0.60 = \frac{\pi}{4} d^2$$

$$d^2 = 0.765$$

$$d = 0.875 \text{ ft} = 10.5 \text{ in.}$$

∴ use 1 ft diameter

H2O spray onto the marble bed

Use 10 gal/1,000 cf x 300 cfm = 3 gal/min of H_2O

Estimated ΔP will be about 4 in. H_2O

Quenching

Use gas velocity of 500-700 fpm[a]

Gas flow 840 acfm at 1400°F

Desire cooling to ≈ 225°F

$$\left.\begin{array}{l}\text{Enthalpy of air at 1400°F = 342 Btu/lb} \\ \text{Enthalpy of air at 225°F = 40 Btu/lb}\end{array}\right\} \Delta h = 302 \text{ Btu/lb}$$

Avg. Cp of air (1400-200°F) ≈ 0.244 Btu/lb °F

(840 acf/min)(.021 lb/acf) = 18 lb/min of air

Cooling reqd. = (18 lb air/min)(302 Btu/lb) = 5,500 Btu/min

Heat absorbed by water ≈ 1,100 Btu/lb H_2O

$$\therefore \text{ Water reqd.} = \frac{5{,}500 \text{ Btu/min}}{1{,}100 \text{ Btu/lb } H_2O} = 5 \text{ lb/min of } H_2O$$

∴ Use 1 gal/min H_2O

Table 21. (Continued)

Velocity of gas entering quench section (12 in. pipe) is:

Area of 12 in. pipe = 0.78 ft^2

$$\frac{840 \text{ acf/min}}{0.78 \text{ ft}^2} = 1{,}100 \text{ ft/min}$$

Velocity out: $$\frac{300 \text{ acf/min}}{0.78} = 390 \text{ ft/min}$$

$\therefore$ that avg. velocity through Quench section using 12-in. pipe will be o.k. compared to desired 500-700 fpm above.

Calculate diameter of demisters

$$\text{Optimum design velocity} = 0.35\sqrt{\frac{\rho_L - \rho_G}{\rho_G}}$$

$$= 0.35\sqrt{\frac{62.4 - 0.07}{0.07}}$$

$$= 0.35\sqrt{890}$$

$$= 0.35\ (29.8) = 10.4 \text{ ft/sec} \times 60 = 600 \text{ ft/min optimum design velocity}$$

300 cfm/3 ft^2 = 100 ft/min

Gas flow design basis = 300 acfm

Use demister pad dia. of 12 in.

$$\therefore \text{Face velocity} \cong \frac{300 \text{ ft}^3\text{/min}}{1 \text{ ft}^2} = 300 \text{ ft/min}$$

2. Scrubber No. 2
Design of second stage scrubber (hexylene glycol)

Density of hexylene glycol = 0.97; assume viscosity ~ that of ethylene glycol

Use liquid flow of 8 gpm

$$\therefore \frac{L}{G}\sqrt{\frac{\rho_G}{\rho_L}} = 0.10 \xrightarrow{\text{then}} \text{Read } f(G^1)^2 = 0.10$$[a]

Table 21. (Continued)

$U_2' =$ ethylene glycol 15 cp $\qquad (15)^{0.2} = 1.7$

$$0.10 = \frac{(G^1)^2 \frac{a}{E^3} U^{0.2}}{gc\ \rho_G\ \rho_L}$$

$$(G^1)^2 = \frac{0.10\ gc\ \rho_G\ \rho_L}{\frac{a}{E^3} \quad U^{.2}}$$

$$(G^1)^2 = \frac{(0.10)(32.2)\overset{\rho_G}{(0.07)}\overset{PR}{(60)}}{(400)(1.7)} = 0.020$$

$G^1 = 0.141$ lb/sec ft^2 gas flow at flooding

gas flow - 0.38 lb/sec

$$\text{Area reqd.} = \frac{0.38\ \text{lb/sec}}{0.141\ \text{lb/sec ft}^2} = 2.7\ \text{ft}^2 \text{ at flooding}$$

Use 4.0 ft^2 to be below flooding
$\therefore$ 27 in. diameter

3. Scrubber No. 3
Design of third stage H_2O scrubber

Basis: 250 acfm at 100°F

Not possible to calculate the quantity of water required to remove carry-over of hexylene glycol, therefore, use 8-10 gal/1,000 cf or 2 gpm.

Calculate tower diameter required

$$\frac{L'}{V'}\left(\frac{\rho_G}{\rho_L}\right) 0.5 \qquad [a]$$

$L' = 2$ gal/min x 60 x (8.34 lb/gal) = 1,000 lb/hr

$V' =$ (18 lb air/min + 5 lb/min H_2O)(60) = 1,400 lb/hr

Table 21. (Continued)

Area reqd. $= \dfrac{0.38 \text{ ft/sec}}{0.276 \text{ lb/sec ft}^2} = 1.4 \text{ ft}^2$ at flooding

Est use 2.0 ft^2 21 in. Ø

$$\frac{L}{G}\sqrt{\frac{\rho_G}{\rho_L}} = 0.025 \text{ (pg3)}$$

For 1/2 in Raschig rings b/

Irrigation rate = 0.9 gal/min ft^2

$$\frac{2 \text{ gal/min}}{0.9 \text{ gal/min ft}^2} = 2.2 \text{ ft}^2$$

Considering recommended value of 5 gpm/ft^2 recalculate tower dia.

Increase from 2 gpm up to 8 gpm

$$\therefore \frac{L}{G}\sqrt{\frac{\rho_G}{\rho_L}} = 0.10 \qquad \text{b/}$$

Read new value of 0.10a/ compared to 0.20b/

$$(G^1)^2 = \frac{(0.10)(32.2)(0.07)(62.4)}{(400)(0.93)}$$

$$(G^1)^2 = 0.038$$

$G^1 = 0.195 \text{ lb/sec ft}^2$ gas flow at flooding

gas flow = 0.38 lb/secb/

Area reqd. $= \dfrac{0.38 \text{ lb/sec}}{0.195 \text{ lb/sec ft}^2} = 2.0 \text{ ft}^2$ at flood

Use 3.0 ft^2 to be below flooding
2 ft Ø or 24 in.

∴ Use 24 in. dia. vessel with 4 spray nozzles, each of which deliver 2 gpm for a total water flow of 8 gpm.

Table 21. (Concluded)

satrd. air at 100°F = 15 ft^3/lb dry air

0.04 lb H_2O/lb air

15 ft^3/1.04 lb $\therefore \rho_G = 0.070$ lb/ft^3

$\rho_L = 62.4$ lb/ft^3

$$\frac{L'}{V'}\left(\frac{\rho_G}{\rho_L}\right)^{0.5} = \frac{1,000}{1,400}\sqrt{\frac{0.070}{624}} = \frac{1,000}{1,400}(0.035) = 0.025$$

Read value of 0.20[a]

$$\frac{(G^1)^2 \left(\frac{a}{E^3}\right)(U_2')^{0.2}}{gc\ \rho_G\ \rho_L} = 0.20$$ [a]

G^1 = gas flow lb/sec ft^2

$\frac{a}{E^3} = 400$

U_2' = liquid viscosity cp = 0.70 cp (0.70)0.2 = 0.93

gc = 32.2

$\rho_G = 0.07$ lb/ft^3

$\rho_L = 62.4$ lb/ft^3

$$(G^1)^2 = \frac{(0.20)(gc\ \rho_G\ \rho_L)}{\left(\frac{a}{E^3}\right)(U_2')0.2} = \frac{(0.20)(32.2)(0.07)(62.4)}{(400)(0.93)}$$

$(G^1)^2 = 0.076$

$G^1 = 0.276$ lb/sec ft^2 gas flow at flooding point

gas flow = (23 lb/min)(min/60 sec) = 0.38 lb/sec

---

[a] Danielson, John A., Air Pollution Engineering Manual, U.S. Department of Health, Education, and Welfare, Public Health Service, Publication No. 999-AP-40, Cincinnati, Ohio (1967).

[b] Clarke, Loyal, Manual for Process Engineering Calculations, McGraw-Hill Book Company, Inc., New York, New York (1947).

Scrubber No. 1 was a water scrubber designed to cool the stack gases and remove the contained particulate matter. Located above the collection tank in the downcoming stack were two 1 gpm nozzles. The gas then passed through a marble bed with a third nozzle washing the bottom of the bed. The marble bed had eight downcomers, with outlets beneath the collected water surface. The downcomers were used to eliminate foam above the marble bed. Just before exiting Scrubber No. 1, the gases passed through a 12-in. diameter, 4 in. thick 304 stainless steel demister pad. Water collected in the main body of the scrubber, a 2 ft by 4 ft oval tank, and drained by gravity through a water trap to a sump pump. The sump pump transferred the water to a temporary holding tank for sampling.

The main body of hexylene glycol Scrubber No. 2 was a 28 in. diameter by 8 ft high. The gases from Scrubber No. 1 entered beneath a 2 ft deep bed of 1/2 in. raschig rings. Four spray nozzles of 2 gpm each sprayed down on the rasching rings. Gases from Scrubber No. 2 passed through another demister pad located as in the first scrubber. The hexylene glycol collected in the bottom of the scrubber for recycle through the spray system.

Scrubber No. 3 was similar to Scrubber No. 2. The raschig ring bed was 1 ft deep and water was used as the scrubbing liquid. Water collected in the bottom of the scrubber for removal by gravity to a sump pump transferring the water to a temporary hold tank. Water collected in the hold tank was sampled and analyzed. The main body of Scrubber No. 3 was 24 in. in diameter and 7 ft high.

SCRUBBER WATER TREATMENT SYSTEM

The system used to treat the scrubber waters is shown in Figure 19. Water from Scrubbers Nos. 1 and 3 was collected during the experimental test in separate hold tanks inside Building No. 1 for sampling and analysis. This water was then pumped outside to larger hold tank before treatment and disposal. Approximately 800 gal. were collected during each experimental test.

From the outside hold tank, the scrubber water was pumped to a sand filter for removal of particulate matter. Flow to the sand filter was controlled by two float switches, one on the outside hold tank and another on the sand filter.

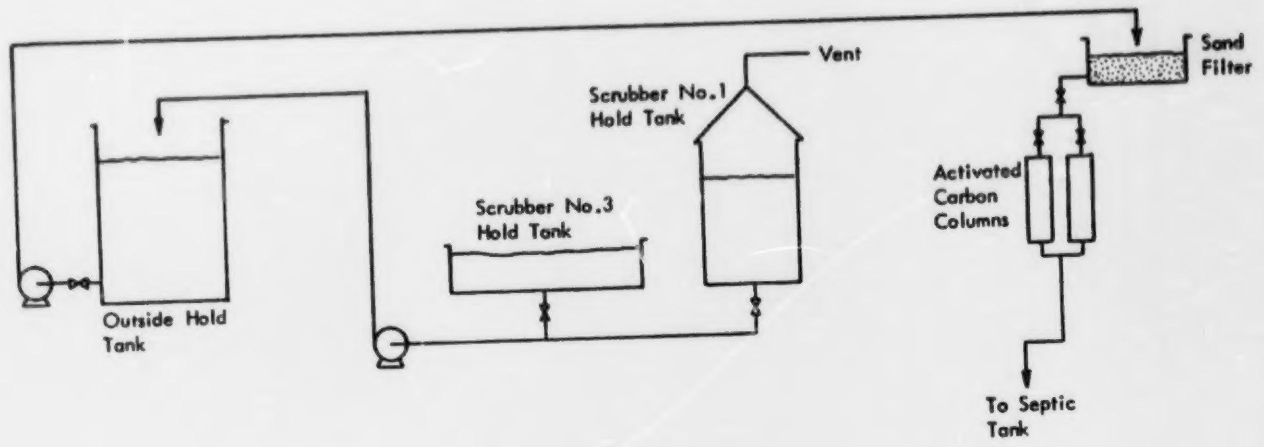


Figure 19. Scrubber water treatment system

Water flowed by gravity through a filter composed of two layers of media; the top was filter sand 6 in. in depth and the bottom, limestone chat, 1/4 in. nominal diameter, 6 in. deep.

The filtered water then passed through two parallel columns 8 in. in diameter and 4 ft high. These columns contained approximately 25 lb (dry weight) each of 6 to 8 mesh activated carbon.

Effluent from the carbon columns was discharged into the facility septic tank system.

ANCILLARY EQUIPMENT

Table 22 lists other equipment used as part of the experimental system.

Table 22. ANCILLARY EQUIPMENT

Designation	Make	Model	Purpose
Fuel oil pump	American Gear	77	Transfer fuel oil from storage to the feed system
Burner	Ray (Monarch and Steinen nozzles)	1XPJ	Fuel oil burner 3.0 to 8.0 gal/hr
Burner	Wondaire (Monarch and Steinen nozzles)	OE	Fuel oil burner 0.6 to 3.0 gal/hr
Burner	Wondaire	PG-260B	Natural gas burner
Firebrick	Kaiser Refractories	Morex	
Thermocouples	Chromel-Alumel	22 gauge	
Manometer	Dwyer 172		Manometer No. △1
Manometer	Dwyer 171		Manometer No. △2
Spray nozzles	Spraying Systems	1/2 GG3030 3/8 GG15 1/8 GG5	2 gal/min 3 gal/min 1 gal/min
Demister pad	York	304 stainless steel	4-in. thickness 12-in. diameter
Sump pumps	Little Giant	8 CIA	Transfer water from the scrubbers to the hold tanks
Hexylene glycol pump	Weinman	5ACK-10P	Recycle the hexylene glycol
Raschig rings	Knight	ceramic	1/2-in. diameter 1/2-in. length
Blower	New York Blower	Size 12	Induce draft
Liquid pesticide pump	Oberdorfer	C-6287	Inject water-based liquid pesticides

Table 22. (Concluded)

Designation	Make	Model	Purpose
Vibrating screw feeder	Vibra Screw		Feed solid pesticides
Temperature recorder	Leeds and Northrup	Speedomax W	12 points variable chart speed
Total hydrocarbons analyzer	Beckman	6800	
Total hydrocarbons recorder	Leeds and Northrup	601	
Particulate sampling consol	Research Appliance Corp.	2343-10	
Discharge pump	Meyers	100M1/2	Transfer water from the scrubber hold tanks
Outside hold tank pump	Stayrite	JH1B	Transfer water to the filter
Scales	Fairbanks-Morse	0-500 lb	Weighing and mixing pesticide formulations

APPENDIX B

TEST RESULTS

CONTENTS

Page

I. DDT. 117

Pesticide Description. 117
Formulations Tested. 119
Preliminary Thermal Analyses 120
Methods of Analysis. 121
Test Conditions and Results. 124
Discussion 143
References 144

II. Aldrin 145

Pesticide Description. 145
Formulations Tested. 146
Preliminary Thermal Analysis 148
Methods of Analysis. 153
Test Conditions and Results. 154
Discussion 167
References 168

III Picloram 169

Pesticide Description. 169
Formulations Tested. 170
Preliminary Thermal Analysis 171
Methods of Analysis. 177
Test Conditions and Results. 180
Discussion 197
References 198

Preceding page blank

CONTENTS (Continued)

Page

IV. Malathion. 199

Pesticide Description. 199
Formulations Tested. 204
Preliminary Thermal Analysis 205
Methods of Analysis. 208
Test Conditions and Results. 212
Discussion 223
References 224

V. Toxaphene. 225

Pesticide Description. 225
Formulations Tested. 227
Preliminary Thermal Analysis 228
Methods of Analysis. 233
Test Conditions and Results. 238
Discussion 250
References 251

VI. Atrazine 252

Pesticide Description. 252
Formulations Tested. 253
Preliminary Thermal Analysis 254
Methods of Analysis. 262
Test Conditions and Results. 265
Discussion 278
References 279

VII. Captan 280

Pesticide Description. 280
Formulations Tested. 283
Preliminary Thermal Analysis 283
Methods of Analysis. 284
Test Conditions and Results. 290
Discussion 296
References 297

CONTENTS (Concluded)

Page

VIII. Zineb. 298

Pesticide Description. 298
Formulations Tested. 299
Preliminary Thermal Analysis 300
Methods of Analysis. 306
Test Conditions and Results. 309
Discussion 316
References 318

IX. Mirex. 319

Pesticide Description. 319
Formulations Tested. 320
Preliminary Thermal Analysis 321
Methods of Analysis. 321
Test Conditions and Results. 325
Discussion 333
References 334

This appendix contains a summarization of data from the pilot scale incineration of representative commercial formulations of nine pesticides. The rationale for the pesticides' selection, as well as the experimental design used for their study, have been discussed in detail in Sections III and IV, respectively, of the main text of the report.

The experimental facilities used for these tests have been reviewed in Appendix A, and are shown in Figure 1, p. 21. The sample points, thermocouple positions, and manometer locations referenced in the following discussions are shown in Figure 5, p. 27.

I. DDT

PESTICIDE DESCRIPTION

Physical Properties

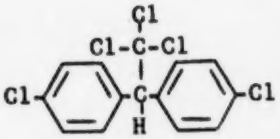
Chemical Name: 1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane; dichloro diphenyl trichloroethane

Common Name: DDT

Trade Names: Anofex®, Chlorophenotane®, Dedelo®, Dicophane®, Genitox®, Gesapon®, Gesarex®, Gesarol®, Gyron®, Ixodex®, Kopsol®, Neocid®, Pentachlorin®, Rukseam®, Zerdane®

Pesticide Class: Broad spectrum insecticide; chlorinated hydrocarbon

Structural Formula:



Empirical Formula: $C_{14}H_9Cl_5$

Molecular Weight: 354.3

Physical State: White, crystalline solid

Characteristics: Technical grade DDT contains a mixture of p,p'-isomers, o,p'-isomers, as well as related chlorinated compounds. Domestically produced technical grade DDT contains 75 to 80% p,p'-isomers, and 15 to 20% o,p'-isomers (Lawless et al.1/). FAO specifications (of the Food and Agriculture Organization of the United Nations) require a minimum p,p'-DDT content of 70% (von Rümker and Horay2/).

For purposes of this report, "DDT" has been defined to include four major isomers commonly found in the technical material; i.e., p,p'-DDT, o,p'-DDT, p,p'-DDE, and o,p'-DDE. Both o,p'-DDD and p,p'-DDD have been arbitrarily included with the "other" chlorinated hydrocarbon species.

Melting Point: 108.5 C (p,p'-DDT)

Boiling Point: Decomposes at 110° C (von Rümker and Horay)[2]

Specific Gravity: 1.38 (technical grade); 1.6 (p,p'-isomer)

Vapor Pressure: 1.9×10^{-7} mm Hg at 20° C (p,p'-DDT)

Chemical Properties

Zeidler[3] discovered that DDT undergoes a dehydrochlorination reaction in strongly basic solution, i.e., caustic alkali in alcohol, to give a product now known as DDE.

$$(ClC_6H_4)_2CH\text{-}CCl_3 \quad \substack{\text{Base}\\ \text{Alcohol}} \quad (ClC_6H_4)_2C{=}CCl_2 + HCl\cdot Base$$

Dehydrochlorination was shown to be complete in 30 to 60 min at room temperature in 0.1N alkali solution by Wain and Martin[4] and also to occur with organic bases such as amines by Lord.[5]

DDT is quite resistant to oxidation and is not oxidized by chromic oxide in glacial acetic acid or by nitric acid, although the latter nitrates the aromatic rings, according to Fleck[6] and Beilstein's Handbuch der Organischen Chemie.[7] Similarly, attempted oxidation by permanganate, persulfate, chlorine or hypochorite has given poor results.[8]

The reduction of DDT by active metals has been known for several years. For example, a mixture with zinc granules and HCl in aqueous ethanol gives a mixture of partially dechlorinated products: $(ClC_6H_4)_2CH\text{-}CH_3$, $(ClC_6H_4)_2\text{-}CH\text{-}CHCl_2$, and $ClC_6H_4\text{-}CH{=}CH\text{-}C_6H_4Cl$, as referenced in Beilstein's Handbuch der Organischen Chemie.[7]

Putnam et al.[9] reported DDT to be stable up to about 300° C, and at this temperature at least 10% of the DDT distilled without decomposition. Only 5% of the DDT distilled when the pyrolysis was conducted in the presence of mineral oil and only 1% with potassium chlorate, but unfortunately the decomposition products, some of which appear to be chlorinated hydrocarbons, were not identified.

Molten DDT is subject to catalytic dehydrochlorination by impurities, such as certain metals as shown by Fleck.[6]

The incineration of DDT in a kerosene carrier has been studied by Whaley et al.[10]/ at the Canadian Combustion Research Laboratories in Ottawa. Whaley's work has shown that a DDT-kerosene formulation can be "completely" destroyed in an incinerator utilizing a commercially available blue-flame burner. This study provided the design data from which the Canadian Department of National Defense built and operated a special incineration system to destroy 107,000 gal. of a kerosene-based DDT formulation.[11]/ Further, study by Lee et al.[12]/ has shown that a DDT dust formulation can be similarly destroyed.

Production and Use

The registrations for essentially all domestic uses of DDT have been cancelled. However, DDT is still being manufactured in the United States by one company, primarily for export to other countries. The estimated annual production rate in 1972 was 45 million pounds (Lawless et al.[1]/).

FORMULATIONS TESTED

Two major formulations of DDT were tested: a 2 lb/gal (25%) emulsifiable concentrate (EC), and a 10% DDT dust.

4 lb/gal EC

Name: AMOCO® elm spray emulsifiable DDT concentrate

Manufacturer: American Oil Company, Chicago, Illinois

Composition: Active ingredients (by weight)

Dichloro diphenyl trichloroethane (DDT)	25%
Petroleum oil (a paraffinic horticultural oil)	18%
Xylene (boiling range 270-290°F)	55%
Inert ingredients (by weight)	2%
Total	100%

Registration: USDA Reg. No. 1145-8

Lot No.: F-039-013-26B

10% Dust

Name: Tobacco States Brand 10% DDT Ready Mixed Dust

Manufacturer: Tobacco States Chemical Company, Lexington, Kentucky

Composition:	Active ingredient	
	Dichloro diphenyl trichloroethane (DDT)	10.00%
	Inert ingredients	90.00%

Registration: USDA Reg. No. 226-59

Particle Size Specifications: Manufactured from a mixture of 20 parts (by weight) of a 50% DDT dust (10 parts technical DDT and 10 parts attapulgite ground to < 44 μ (325 mesh) and 80 parts soapstone (< 74 μ (200 mesh)).

PRELIMINARY THERMAL ANALYSES

The heat of combustion of the 25% EC formulation was determined at the outset of the study. The results were as follows:

Heat of combustion	3.4676×10^7 J/kg	(14,921 Btu/lb)
Sulfur		1.16%

Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were not conducted for DDT. Other investigations, however, have reported the results of such analyses. Kennedy et al.[13] reported temperatures at which endothermic and exothermic peaks were observed for analytical standard and technical flake DDT. The results of their tests were as follows:

	Endotherms	Exotherms
Reference standard	60, 110, 180 and 350°C	545°C
Technical flake DDT	70, 110, 240, 275 and 355°C	375, 578, and 825°C

Sensitivity = 25%.

Based on these and other laboratory analyses, Kennedy et al. concluded that the temperature of complete combustion for the DDT reference standard and technical material were 560°C (1040°F) and 850°C (1560°F), respectively.

Putnam et al.[9] also studied the combustion of DDT in a closed system, i.e., samples encapsulated in a volatile sample pan, using differential scanning calorimetry (DSC). These tests showed decomposition over the range of 305 to 325°C. DSC of DDT open to the air, however, did not show exotherms. The authors concluded that their test results indicate that pesticides heated in an open system apparently do not decompose, but vaporize or sublime (combustion of DDT was reported to have been observed at 182°C).

METHODS OF ANALYSIS

Apparatus

A Micro-Tek 2000R gas chromatograph equipped with a 3-ft, 4 mm I.D. glass column (packed with 1.5% OV-17 + 1.95% QF-1 on 80/100 mesh Supelcoport from Supelco, Inc., Bellefonte, Pennsylvania) and a tritium electron capture detector, maintained at a voltage of 15 V DC, was used for gas chromatographic analysis. Chromatographic operating conditions were: injection temperature 225°C; column temperature, 200°C; detector temperature, 180°C; carrier flow rate, 100 ml/min, N_2; and purge gas flow rate, 200 ml/min, N_2.

A Honeywell strip chart recorder was used to record the chromatograms.

Reagents and Materials

The solid standards o,p'-DDT (99+%), p,p'-DDT (99+%), o,p'-DDE (99%), p,p'-DDE (99%), o,p'-DDD (99%), and p,p'-DDD (99%) used for preparing stock standard solutions (as well as standards for all other pesticides tested) were obtained from the Pesticides and Toxic Substances Effects Laboratory, USEPA, Research Triangle Park, North Carolina. Solvents used were pesticide grade benzene (Fisher Scientific) for standard solutions and extraction of water samples and residues, and pesticide grade hexane (Matheson, Coleman, and Bell) for extraction of hexylene glycol samples (from the second stage scrubber). All laboratory glassware (beakers, vials, pipettes, etc.) was washed in Alconox detergent (Scientific Products) and rinsed with deionized, distilled water and reagent grade acetone (Fisher Scientific).

Standards and Calibration Curves

The solid standards o,p'-DDT, p,p'-DDT, o,p'-DDE, p,p'-DDE, o,p'-DDD, and p,p'-DDD obtained from USEPA, were used to prepare separate stock standards of 100 μg/ml each and appropriate dilutions were made of each to produce a linear curve (linear range used on each: 0 to 500 pg).

Procedure for Sample Preparation

In all tests involving the 25% EC formulation, the samples collected in water were extracted with two 5-ml portions each of benzene; 10 ml of the hexylene glycol samples (second stage scrubber) were extracted with two 5-ml portions of hexane. Appropriate amounts (1 to 5 μl) of the extracted samples and the samples collected in benzene impingers were injected into the gas chromatograph.

The mass of collected particulate was determined for all samples collected from incineration of DDT dust (Runs A through H) as follows: samples were taken to dryness in clean, dessicated, tared 250-ml beakers and dessicated 2 days before final weighing. The residues were extracted with benzene (10 or 20 ml depending on amount of residue) and appropriate portions of these extracts were injected for analysis. The silica gel impinger was extracted with known volume of benzene to cover the solid and a portion of the extract was analyzed. Benzene blanks were analyzed directly as they came from the field. A portion of water blanks was extracted with known volume of benzene and the extract was analyzed by gas chromatography.

Portions of all the cleanout samples (primary chamber, secondary chamber, etc.) were weighed out, extracted and the extracts analyzed for DDT and its isomers.

Analysis and Discussion

All samples were analyzed for DDT, and its isomers. Unidentified chromatographic peaks were quantitated against the p,p'-DDT calibration curves. A representative chromatogram for the 25% EC DDT formulation is shown in Figure 20.

The sensitivities of the instrument for DDT and its isomers were: 5 pg for p,p'-DDT, 5 pg for o,p'-DDT, 2 pg for p,p'-DDE, 5 pg for o,p'-DDE, 10 pg for p,p'-DDD, and 10 pg for o,p'-DDD. Based on these sensitivity values, and with a 5 μl sample injection for each analysis, the

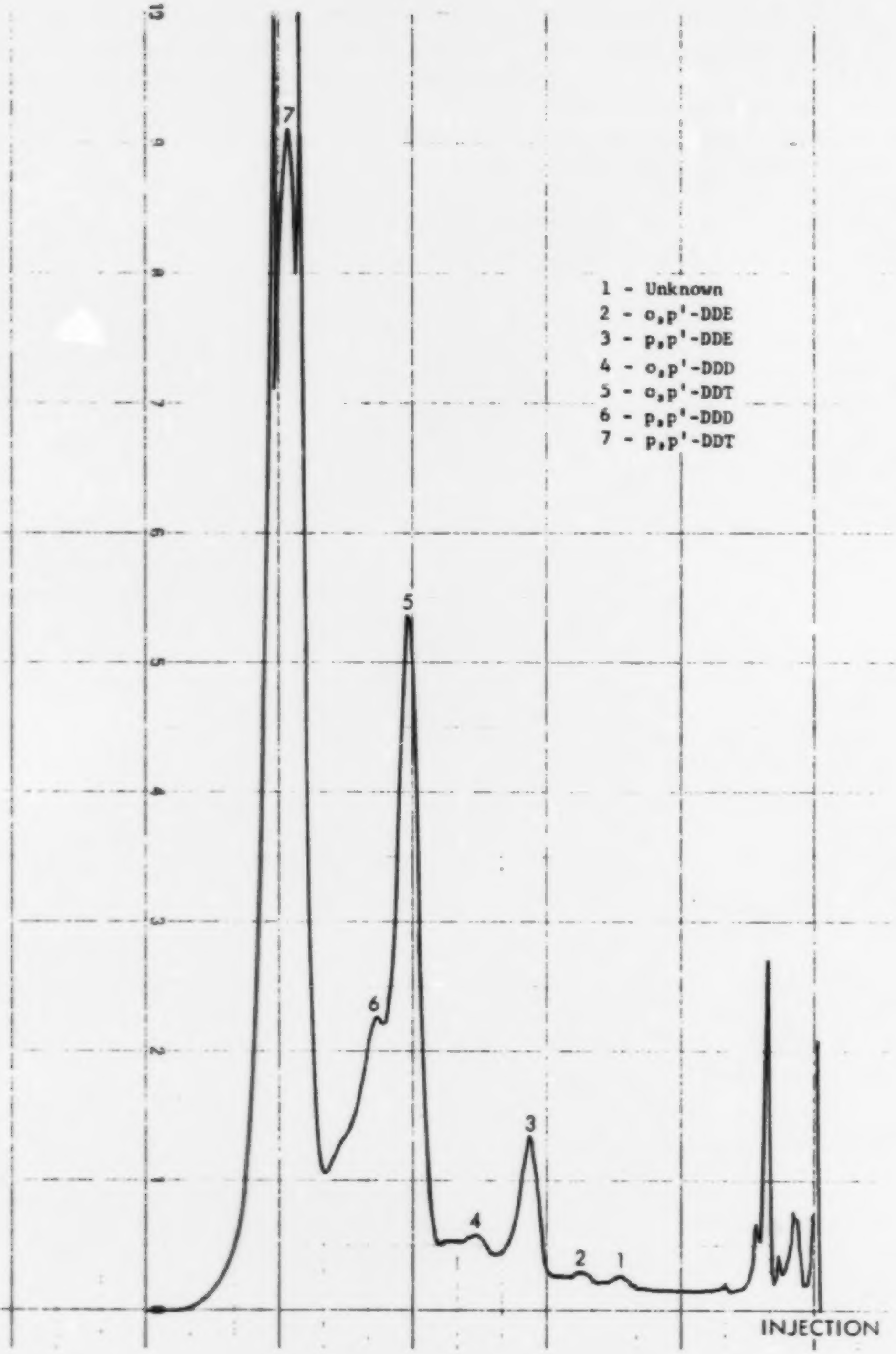


Figure 20. Representative chromatogram of 25% EC DDT formulation

minimum detectable values for a 20-ml sample solution were 20 ng for p,p'-DDT, 20 ng for o,p'-DDT, 8 ng for p,p'-DDE, 20 ng for o,p'DDE, 40 ng for p,p'-DDD and 40 ng for o,p'-DDD. However, during the analysis, samples were very often concentrated down to 1 ml, which resulted in minimum detectable quantities of 1 ng for p,p'-DDT, 1 ng for o,p'-DDT, 0.4 ng for p,p'-DDE, 1 ng for o,p'-DDE, 2 ng for p,p'DDD, and 2 ng for o,p'-DDD.

TEST CONDITIONS AND RESULTS

DDT was specified as the first pesticide to be studied. The combustion of DDT, which represents one of the most acute disposal problems, has been the subject of several research studies. The first experiment, therefore, was intended not only to provide data on combustion of this pesticide, but also to provide a means for relating our findings to those from other research programs.

There are a number of factors that can influence the operation of an incinerator. These include pesticide injection rate, operating temperature, air flow rate, turbulence, auxiliary fuel rate, and retention time. The interaction of many of these factors, however, is such that they cannot all be independently varied. Pesticide injection rate, excess air rate, operating temperature, and turbulence were selected as the variables to be independently varied during the DDT experiments. Retention time and supplemental fuel rate, therefore, were dependent (concomitant) variables.

A modified fractional factorial experiment was designed to study the combustion of liquid (25% EC) formulation. The four controlled variables (each at two levels) were run in 16 combinations (see Table 23).

Pesticide Injection Rate

The 25% EC formulation was initially injected at a nominal rate of 3.4 kg (7.5 lb) DDT per hour. The second level of DDT injection was one-half of the initial rate. A standard fuel oil burner was used as the pesticide injection system.

Excess Air

Air was injected at approximately 50 and 150% excess, calculated according to Method 3 of "Standards of Performance for New Stationary Sources," Federal Register, 36(247):24876-24895, 23 December 1971.

Table 23. FACTORIAL DESIGN FOR 25% DDT EC EXPERIMENT

Experiment Designation	Turbulence	Pesticide Injection Rate	Operating Temperature	Excess Air Rate
A	a	c	e	g
B	a	c	e	h
C	a	c	f	g
D	a	c	f	h
E	a	d	e	g
F	a	d	e	h
G	a	d	f	g
H	a	d	f	h
I	b	c	e	g
J	b	c	e	h
K	b	c	f	g
L	b	c	f	h
M	b	d	e	g
N	b	d	e	h
O	b	d	f	g
P	b	d	f	h

a - frontal configuration
b - side configuration
c - 1.70 kg (3.75 lb) DDT per hour
d - 3.4 kg (7.5 lb) DDT per hour
e - 950°C (1750°F)
f - 1090°C (2000°F)
g - 50%
h - 150%

Temperature

The incinerator temperature was to be varied from approximately 950°C (1750°F) to 1090°C (2000°F), i.e., the nominal operating range of the experimental incinerator with the available fuel oil burner. The temperature was obtained by injecting the desired amount of DDT (in the EC formulation) mixed with the appropriate amount of supplemental fuel (No. 2 fuel oil).

Turbulence

Turbulence within the ignition chamber is influenced by the location and orientation of the supplemental fuel and pesticide injector as well as by any internal baffling. Two levels of "turbulence" were studied by injecting the EC formulation through the fuel oil burner in the front (primary) and in the side (alternate) position of the primary combustion chamber (see Figure 1, p. 21).

A total of 21 tests were conducted to fit the 16 points of a modified fractional factorial analysis of the parameters (combustion chamber turbulence, rate of operation, operating temperature, and excess air rate).

Results of these tests are summarized in Tables 24 through 27. The incineration efficiencies given in Table 25 are those for the incinerator portion of the pilot scale system only, i.e., DDT discharged from the incinerator stack (Sample Point No. ②), versus DDT charged into the incinerator (Sample Point No. ① , Figure 5, p.27). Samples from Sample Point No. ③ (solid residue in the combustion chambers) do not enter into the efficiency calculations because no solid residue was generated by the liquid formulations.

Two efficiencies were calculated in order to better evaluate the completeness of combustion. The first, shown in the next to last column of Table 25, is based only on the four major constituents of technical "DDT," which for purposes of this report, have been defined as DDT, i.e., p,p'-DDT, o,p'-DDT, p,p'-DDE, o,p'-DDE. The second efficiency includes not only these four constituents but also all "other" species collected in the respective samples. This "other" category includes various chlorinated hydrocarbons having a lower molecular weight and higher volatility than p,p'-DDT, including p,p'-DDD and o,p'-DDD.

The data in Table 24 clearly show that we were not able to operate the incinerator at the desired levels for each independent variable. For this reason, the data could not be strictly evaluated as representing a fractional-factorial experiment.

Table 24. SUMMARY OF 25% DDT EC EXPERIMENTS

Experiment designation	Incinerator feed rate					Turbulence[c]	Primary chamber temperature °C (°F)	Excess air[d] %	Retention time sec[e]		Sampling time min	Off-gas flow rate,[f] m³/hr (1,000's of SCFH)
	Nominal burner size ℓ/hr (gal/hr)	Total feed rate ℓ/hr (gal/hr)	DDT rate g/hr (lb/hr)[a]	DDT rate ℓ/hr (gal/hr)[b]	No. 2 fuel oil rate ℓ/hr (gal/hr)				Primary chamber	Second chamber		
A	11.3 (3.0)	9.39 (2.48)	1,090 (2.42)	4.67 (1.18)	4.92 (1.30)	1	1040 (1900)	92	2.5	2.7	30	218 (7.7)
B	13.2 (3.5)	15.59 (4.12)	1,910 (4.23)	7.91 (2.09)	7.68 (2.03)	1	940 (1730)	162	1.3	1.2	28	419 (14.8)
C	13.2 (3.5)	15.44 (4.08)	1,950 (4.27)	7.99 (2.11)	7.46 (1.97)	1	1140 (2090)	88	1.6	1.8	30	326 (11.5)
	13.2 (3.5)	11.66 (3.08)	1,770 (3.88)	7.23 (1.91)	4.63 (1.17)	1	1170 (2130)	100	1.5	1.6	30	343 (12.1)
D	24.6 (6.5)	24.07 (6.36)	1,630 (3.59)	6.70 (1.77)	17.37 (4.59)	1	1040 (1900)	120	0.9	0.7	30	643 (22.7)
E	11.3 (3.0)	9.39 (2.48)	1,320 (2.90)	5.41 (1.43)	3.97 (1.05)	1	1050 (1930)	85	2.4	2.4	30	229 (8.1)
F	18.9 (5.0)	20.36 (5.38)	4,630 (10.25)	20.36 (5.38)	-0-	1	930 (1700)	143	1.0	0.8	30	663 (23.4)
G	13.2 (3.5)	13.32 (3.52)	2,400 (5.29)	9.88 (2.61)	3.44 (0.91)	1	1150 (2110)	116	2.2	2.3	32.5	218 (7.7)
H	24.6 (6.5)	23.88 (6.31)	2,400 (5.34)	9.95 (2.63)	13.93 (3.68)	1	1050 (1920)	135	0.9	0.7	30	648 (22.9)
I	11.3 (3.0)	9.73 (2.57)	1,450 (3.16)	5.90 (1.56)	3.82 (1.01)	2	1070 (1950)	83	2.9	3.0	30	193 (6.8)
J	11.3 (3.0)	9.92 (2.62)	1,220 (2.74)	5.11 (1.35)	4.81 (1.27)	2	980 (1800)	138	3.1	3.2	30	190 (6.7)
	11.3 (3.0)	9.16 (2.42)	1,130 (2.53)	4.73 (1.25)	4.63 (1.17)	2	980 (1800)	128	2.5	2.9	30	187 (6.6)
K	13.2 (3.5)	15.67 (4.14)	1,450 (3.21)	5.98 (1.58)	9.69 (2.56)	2	1170 (2140)	64	1.4	1.4	30	351 (12.4)
L	13.2 (3.5)	14.76 (3.90)	1,500 (3.34)	6.24 (1.65)	8.52 (2.25)	2	1050 (1930)	151	1.4	1.3	31	425 (15.0)
	18.9 (5.0)	14.15 (3.74)	500 (1.09)	2.04 (0.54)	12.11 (3.20)	2	1100 (2010)	137	1.6	1.4	30	368 (13.0)
	18.9 (5.0)	16.43 (4.34)	730 (1.62)	3.03 (0.80)	13.40 (3.54)	2	1090 (2000)	163	1.3	1.3	30	405 (14.3)
M	11.3 (3.0)	9.54 (2.52)	1,860 (4.11)	9.54 (2.52)	-0-	2	1030 (1890)	96	1.5	1.6	30	371 (13.1)
N	11.3 (3.0)	9.73 (2.57)	1,810 (3.96)	9.73 (2.57)	-0-	2	960 (1730)	166	3.0	3.1	30	201 (7.1)
O	13.2 (3.5)	13.59 (3.59)	3,220 (7.08)	13.59 (3.59)	-0-	2	1190 (2180)	80	1.7	1.6	30	275 (9.7)
P	13.2 (3.5)	14.12 (3.73)	3,360 (7.36)	14.12 (3.73)	-0-	2	1030 (1890)	164	1.3	1.2	30	442 (15.6)
	18.9 (5.0)	19.42 (5.13)	1,810 (4.03)	7.53 (1.99)	11.88 (3.14)	2	1050 (1930)	130	1.5	1.3	30	394 (13.9)

---

[a] Actual DDT content of the incinerator feed.

[b] Volume of ~ 25% EC formulation in the fuel oil-pesticide mixture.

[c] 1 = Front burner location; 2 = side burner location.

[d] Calculated according to Method 3 of "Standards of Performance for New Stationary Sources," *Federal Register*, 36(247):24876-24895, 23 December 1971.

[e] Retention time is defined as $\frac{V}{v}$, where v is the wet off-gas flow rate from the incinerator at the respective chamber temperature and pressure, and V is the volume of that chamber.

[f] As dry gas at one atmosphere pressure, and 21.1°C (70°F).

Table 25. INCINERATION EFFICIENCY--25% DDT EC FORMULATION

Experiment designation	DDT feed rate[a] g/hr	DDT content of off-gas g/hr	Ratio of DDT in off-gas to DDT fed	Total species[b] content of off-gas g/hr	Ratio of total species[b] content of off-gas to DDT fed	Incinerator efficiency[c] % DDT	Incinerator efficiency[c] % Total species[b]
A	1,090	5×10^{-3}	5×10^{-6}	3.2×10^{-2}	2.9×10^{-5}	> 99.99	> 99.99
B	1,910	3.4×10^{-2}	1.8×10^{-5}	5×10^{-2}	2.7×10^{-5}	> 99.99	> 99.99
C	1,950	1.0×10^{-2}	4.9×10^{-6}	2.5×10^{-2}	1.2×10^{-5}	> 99.99	> 99.99
	1,770	1.5×10^{-2}	9×10^{-6}	3.8×10^{-2}	2.1×10^{-5}	> 99.99	> 99.99
D	1,630	1.7×10^{-1}	1.1×10^{-4}	2.9×10^{-1}	1.7×10^{-4}	> 99.98	> 99.98
E	1,320	7×10^{-3}	5×10^{-6}	3.9×10^{-2}	3.0×10^{-5}	> 99.99	> 99.99
F	4,630	2.3×10^{-1}	5×10^{-5}	2.5×10^{-1}	5×10^{-5}	> 99.99	> 99.99
G	2,400	7×10^{-2}	2.8×10^{-5}	1.7×10^{-1}	7×10^{-5}	> 99.99	> 99.99
H	2,400	9×10^{-2}	4×10^{-5}	1.2×10^{-1}	5×10^{-5}	> 99.99	> 99.99
I	1,450	4×10^{-2}	2.8×10^{-5}	9×10^{-2}	6×10^{-5}	> 99.99	> 99.99
J	1,220	8×10^{-2}	6×10^{-5}	1.7×10^{-1}	1.4×10^{-4}	> 99.99	> 99.98
	1,130	1.3×10^{-2}	1.2×10^{-5}	2.6×10^{-2}	2.3×10^{-5}	> 99.99	> 99.99
K	1,450	5×10^{-2}	3.5×10^{-5}	1.3×10^{-1}	9×10^{-5}	> 99.99	> 99.99
L	1,500	6×10^{-2}	3.8×10^{-5}	1.8×10^{-1}	1.2×10^{-4}	> 99.99	> 99.98
	500	2.6×10^{-2}	5×10^{-5}	3.0×10^{-2}	6×10^{-5}	> 99.99	> 99.99
	730	3.6×10^{-2}	5×10^{-5}	4.1×10^{-2}	6×10^{-5}	> 99.99	> 99.99
M	1,860	6×10^{-2}	3.4×10^{-5}	1.8×10^{-1}	9×10^{-5}	> 99.99	> 99.99
N	1,810	8×10^{-2}	4.4×10^{-5}	3.0×10^{-1}	1.6×10^{-4}	> 99.99	> 99.98
O	3,220	2.1×10^{-2}	7×10^{-6}	6×10^{-2}	1.8×10^{-5}	> 99.99	> 99.99
P	3,360	8×10^{-2}	2.4×10^{-5}	9×10^{-2}	2.6×10^{-5}	> 99.99	> 99.99
	1,810	5×10^{-2}	3.0×10^{-5}	9×10^{-2}	4.9×10^{-5}	> 99.99	> 99.99

---

a/ Actual DDT content of the incinerator feed.

b/ DDT plus all other chlorinated hydrocarbon species detected.

c/ Efficiency is defined as $\left[1 - \frac{\text{quantity out}}{\text{quantity in}}\right] \times 100$, where the quantity out is evaluated at Sample Point No. ② (the effluent gas), and the quantity in is evaluated at Sample Point No. ① (the incinerator feed). Efficiencies have been calculated based on (a) DDT only, and (b) the total chlorinated hydrocarbons detected at Sample Point No. ②.

Table 26. OFF-GAS COMPOSITION--25% DDT EC LIQUID INCINERATION[a]

					Total hydrocarbons analyzer			Orsat analyzer			
Experiment designation	DDT mg/m^3	Total species[b] mg/m^3	SO_2 mg/m^3	NO_x[c] mg/m^3	Total hydrocarbons ppm	CO ppm	CH_4 ppm	O_2 vol. %	CO_2 vol. %	CO vol. %	Moisture vol. %
A	2.4×10^{-2}	1.4×10^{-1}	180	80	NA[e]	NA	NA	10.3	8.4	0.0	4.0
B	8.1×10^{-2}	1.3×10^{-1}	78	7	NA	NA	NA	13.2	6.0	0.0	14.6
C	3.0×10^{-2}	7.7×10^{-2}	220	ND[d]	NA	NA	NA	10.1	8.5	0.1	3.5
	4.5×10^{-2}	1.1×10^{-1}	110	ND	NA	NA	NA	10.7	8.2	0.0	3.5
D	2.7×10^{-1}	4.5×10^{-1}	93	9	66	32	42	11.7	7.1	0.0	4.0
E	2.9×10^{-2}	1.7×10^{-1}	110	ND	NA	NA	NA	9.9	9.0	0.0	6.3
F	3.5×10^{-1}	3.8×10^{-1}	31	81	43	127	27	12.6	6.9	0.1	0.0
G	3.0×10^{-1}	7.6×10^{-1}	78	3	NA	NA	NA	11.6	7.5	0.2	6.8
H	1.4×10^{-1}	1.9×10^{-1}	93	110	51	18	29	12.3	6.7	0.0	5.4
I	2.1×10^{-1}	4.7×10^{-1}	170	290	NA	NA	NA	9.8	8.9	0.1	3.5
J	4.1×10^{-1}	8.8×10^{-1}	89	80	NA	NA	NA	12.4	6.9	0.0	2.5
	7.0×10^{-2}	1.4×10^{-1}	250	6	NA	NA	NA	12.0	7.1	0.0	22.7
K	1.4×10^{-1}	3.8×10^{-1}	180	64	NA	NA	NA	8.5	9.9	0.0	5.4
L	1.4×10^{-1}	4.2×10^{-1}	100	110	NA	NA	NA	12.5	6.8	0.0	7.0
	7.2×10^{-2}	8.2×10^{-2}	150	80	NA	NA	NA	12.5	6.4	0.0	5.3
	8.9×10^{-2}	9.9×10^{-2}	330	120	NA	NA	NA	13.2	6.2	0.0	9.8
M	1.7×10^{-1}	4.7×10^{-1}	92	200	NA	NA	NA	10.6	8.4	0.1	6.8
N	4.1×10^{-1}	1.4	34	56	NA	NA	NA	13.2	6.2	0.0	3.5
O	7.8×10^{-2}	2.1×10^{-1}	50	95	NA	NA	NA	9.5	9.5	0.0	13.9
P	1.8×10^{-1}	2.0×10^{-1}	20	78	NA	NA	NA	13.2	6.4	0.0	8.6
	1.3×10^{-1}	2.3×10^{-1}	95	20	NA	NA	NA	12.1	6.9	0.0	3.9

---

[a] As dry gas at one atmosphere pressure, and 21.1°C (70°F).

[b] DDT plus all other chlorinated hydrocarbon species detected.

[c] Calculated as NO_2.

[d] Not detected.

[e] No analysis.

Table 27. OPERATIONAL DATA SUMMARY--25% DDT FC EXPERIMENTS

Run No.	A	B	C		D	E	F
Temperature °C (°F)							
Primary chamber (Thermocouple No. ①)	1010 (1850)	900 (1660)	1120 (2050)	1170 (2130)	1000 (1840)	1030 (1890)	890 (1640)
Primary chamber (Thermocouple No. ②)	990 (1820)	740 (1360)	NA[d]	NA[d]	920 (1690)	1000 (1830)	640 (1190)
Primary chamber (Thermocouple No. ③)	1040 (1900)	940 (1730)	1140 (2090)	1170 (2130)	1040 (1900)	1050 (1930)	930 (1700)
Second chamber (Thermocouple No. ④)	850 (1570)	850 (1560)	950 (1740)	990 (1820)	990 (1820)	870 (1600)	920 (1680)
Second chamber (Thermocouple No. ⑤)	570 (1060)	670 (1240)	530 (990)	620 (1150)	870 (1590)	600 (1120)	770 (1420)
Sample Point No. ② (Thermocouple No. ⑥)	330 (620)	490 (920)	390 (740)	470 (880)	650 (1210)	390 (740)	590 (1100)
Pressures							
Draft (Manometer No. △1), pascals (in. H_2O) gauge	17 (0.070)	46 (0.185)	25 (0.100)	26 (0.105)	88 (0.355)	10 (0.040)	58 (0.235)
Burner operation pressure, pascals (psi) gauge	7.9×10^5 (114)	NA[c]	NA[c]	NA[c]	NA[c]	7.9×10^5 (115)	7.9×10^5 (115)
Scrubber liquids[a]							
1st Stage H_2O scrubber							
Volume, ℓ (gal.)	1230 (325)	990 (252)	1150 (304)	1140 (302)	1030 (273)	1300 (343)	1050 (277)
DDT conc., mg/ℓ	3×10^{-3}	3×10^{-3}	ND[e]	5×10^{-3}	3×10^{-3}	1×10^{-3}	4×10^{-3}
Total species conc.,[b] mg/ℓ	3×10^{-3}	3×10^{-3}	ND	5×10^{-3}	3×10^{-3}	1×10^{-3}	4×10^{-3}
2nd Stage hexalene glycol scrubber							
Volume, ℓ (gal.)	115 (30.3)	138 (36.4)	134 (35.4)	134 (35.4)	137 (36.1)	119 (31.4)	126 (33.4)
DDT conc. change, mg/ℓ	ND	3×10^{-2}	ND	6×10^{-2}	5×10^{-3}	ND	ND
Total species[b] conc. change, mg/ℓ	ND	2.1×10^{-1}	ND	8×10^{-2}	5×10^{-3}	ND	ND
3rd Stage H_2O scrubber							
Volume, ℓ (gal.)	1990 (525)	1680 (445)	1890 (500)	1760 (465)	1910 (505)	1970 (520)	1820 (480)
DDT conc., mg/ℓ	5×10^{-3}	5×10^{-3}	4×10^{-3}	1×10^{-3}	ND	2×10^{-3}	$< 1 \times 10^{-3}$
Total species[b] conc., mg/ℓ	5×10^{-3}	5×10^{-3}	4×10^{-3}	1×10^{-3}	ND	2×10^{-3}	$< 1 \times 10^{-3}$

Table 27. (Continued)

Run No.	G	H	I	J		K	L
Temperature °C (°F)							
Primary chamber (Thermocouple No. ①)	1140 (2080)	1000 (1840)	1030 (1880)	950 (1740)	940 (1730)	1100 (2020)	890 (1630)
Primary chamber (Thermocouple No. ②)	1150 (2100)	760 (1400)	970 (1780)	890 (1640)	890 (1630)	1030 (1890)	700 (1300)
Primary chamber (Thermocouple No. ③)	1150 (2110)	1050 (1920)	1070 (1950)	980 (1800)	980 (1800)	1170 (2140)	1050 (1930)
Second chamber (Thermocouple No. ④)	980 (1800)	1020 (1860)	850 (1560)	810 (1490)	740 (1360)	980 (1800)	800 (1470)
Second chamber (Thermocouple No. ⑤)	640 (1190)	880 (1620)	630 (1170)	580 (1070)	420 (790)	730 (1340)	660 (1220)
Sample Point No. ② (Thermocouple No. ⑥)	440 (820)	670 (1230)	330 (620)	350 (670)	290 (560)	450 (840)	440 (830)
Pressures							
Draft (Manometer No. △), pascals (in. H_2O) gauge	22 (0.090)	93 (0.375)	15 (0.060)	27 (0.110)	12 (0.050)	27 (0.110)	31 (0.125)
Burner operation pressure, pascals (psi) gauge	7.4×10^5 (108)	NA[c]	7.7×10^5 (112)	7.7×10^5 (112)	NA[c]	7.9×10^5 (115)	7.7×10^5 (112)
Scrubber liquids[a]							
1st Stage H_2O scrubber							
Volume, ℓ (gal.)	1070 (284)	1080 (286)	1290 (340)	1120 (297)	1240 (327)	1140 (300)	1180 (313)
DDT conc., mg/ℓ	7×10^{-3}	5×10^{-3}	$< 1 \times 10^{-3}$	ND[e]	6×10^{-3}	5×10^{-3}	5×10^{-3}
Total species conc.,[b] mg/ℓ	7×10^{-3}	5×10^{-3}	$< 1 \times 10^{-3}$	ND	2.0×10^{-2}	5×10^{-3}	6×10^{-3}
2nd Stage hexalene glycol scrubber							
Volume, ℓ (gal.)	134 (35.4)	132 (34.9)	121 (31.9)	121 (31.9)	132 (34.9)	123 (32.6)	125 (32.9)
DDT conc. change, mg/ℓ	4×10^{-2}	1.0×10^{-1}	2.9×10^{-1}	1.3×10^{-1}	6×10^{-2}	1.5×10^{-1}	ND[e]
Total species[b] conc. change, mg/ℓ	1.0×10^{-1}	1.0×10^{-1}	3.0×10^{-1}	1.5×10^{-1}	1.0×10^{-1}	2.7×10^{-1}	ND
3rd Stage H_2O scrubber							
Volume, ℓ (gal.)	1910 (505)	2010 (530)	1990 (525)	1930 (510)	2010 (530)	1930 (510)	2010 (530)
DDT conc., mg/ℓ	4×10^{-2}	1×10^{-3}	ND[e]	ND[e]	6×10^{-3}	2×10^{-3}	2×10^{-3}
Total species[b] conc., mg/ℓ	4×10^{-2}	1×10^{-3}	ND	ND	6×10^{-3}	2×10^{-3}	2×10^{-3}

Table 27. (Concluded)

Run No.			M	N	O	P	
Temperature °C (°F)							
Primary chamber (Thermocouple No. ①)	950 (1750)	960 (1760)	990 (1820)	900 (1660)	1100 (2010)	890 (1640)	950 (1740)
Primary chamber (Thermocouple No. ②)	800 (1480)	840 (1540)	940 (1720)	840 (1550)	1050 (1920)	750 (1380)	780 (1440)
Primary chamber (Thermocouple No. ③)	1100 (2010)	1090 (2000)	1030 (1890)	940 (1730)	1190 (2180)	1030 (1890)	1050 (1930)
Second chamber (Thermocouple No. ④)	880 (1620)	850 (1560)	820 (1500)	780 (1440)	1000 (1840)	800 (1470)	930 (1700)
Second chamber (Thermocouple No. ⑤)	740 (1370)	730 (1350)	520 (960)	540 (1000)	760 (1400)	660 (1220)	770 (1410)
Sample Point No. ② (Thermocouple No. ⑥)	540 (1000)	540 (1000)	320 (600)	340 (640)	490 (920)	440 (820)	570 (1060)
Pressures							
Draft (Manometer No. △), pascals (in. H_2O) gauge	40 (0.160)	45 (0.180)	15 (0.060)	30 (0.120)	22 (0.090)	36 (0.145)	45 (0.180)
Burner operation pressure, pascals (psi) gauge	7.6×10^5 (110)	7.6×10^5 (110)	7.6×10^5 (111)	7.7×10^5 (112)	7.9×10^5 (114)	7.6×10^5 (110)	7.6×10^5 (110)
Scrubber liquids[a]							
1st Stage H_2O scrubber							
Volume, ℓ (gal.)	1190 (315)	1160 (307)	1200 (316)	1240 (327)	1230 (325)	1290 (340)	1140 (300)
DDT conc., mg/ℓ	3×10^{-3}	7×10^{-3}	ND[e]	5×10^{-3}	2×10^{-3}	3×10^{-3}	5×10^{-3}
Total species conc.,[b] mg/ℓ	3×10^{-3}	4×10^{-2}	ND	1×10^{-2}	2×10^{-3}	5×10^{-3}	5×10^{-3}
2nd Stage hexalene glycol scrubber							
Volume, ℓ (gal.)	126 (33.4)	133 (35.2)	128 (33.7)	128 (33.7)	124 (32.7)	125 (32.9)	131 (34.7)
DDT conc. change, mg/ℓ	1.2×10^{-1}	1.4×10^{-1}	1×10^{-2}	8×10^{-3}	3.1×10^{-1}	2.8×10^{-1}	5.0×10^{-1}
Total species[b] conc. change, mg/ℓ	1.6×10^{-1}	2.0×10^{-1}	1×10^{-2}	5×10^{-2}	5.1×10^{-1}	4.8×10^{-1}	5.8×10^{-1}
3rd Stage H_2O scrubber							
Volume, ℓ (gal.)	2010 (530)	2010 (530)	1890 (500)	2020 (535)	1990 (525)	1910 (505)	1930 (510)
DDT conc., mg/ℓ	ND	2×10^{-3}	1×10^{-3}	1×10^{-3}	2×10^{-3}	2×10^{-3}	1×10^{-3}
Total species[b] conc., mg/ℓ	ND	6×10^{-3}	5×10^{-3}	6×10^{-3}	3×10^{-3}	4×10^{-4}	1×10^{-3}

---

a/ Scrubber water (Scrubbers Nos. 1 and 3) was used once through, while the hexylene glycol (Scrubber No. 2) was recycled. The concentrations reported for hexylene glycol, therefore, are the concentration changes (increases) detected during the respective tests.

b/ DDT plus all other chlorinated hydrocarbon species detected.

c/ Pressure gauge broken.

d/ Thermocouple not working.

e/ Not detected.

Therefore, these data were evaluated using multiple regression analysis, which is the more appropriate statistical technique in this instance because of the uniformly high combustion efficiencies observed in our experiments. Regressions of the four quantitative variables (pesticide injection rate, retention time, temperature, and excess air) were run using: (a) the relative amount of DDT not destroyed ("Ratio of DDT in Off-Gas to Total DDT Fed" column of Table 25); and (b) the relative amount of chlorinated hydrocarbon species not destroyed ("Ratio of Total Species Content of Off-Gas to DDT Fed" column of Table 25).

A multiple regression model, such as $y_i = \alpha_0 + \alpha_1 X_{1i} + \alpha_2 X_{2i} + \alpha_3 X_{3i} + \alpha_4 X_{4i} + C_i$, was used to perform an analysis of variance (ANOVA) in order to furnish values (F-values) which could be used to decide whether or not predicting y_i (relative efficiencies of combustion) by using the model results in significantly more accurate results than "predicting" y_i by random choices from the y_i distribution.

Specifically, the F-value is a ratio of the variance of the y's to the variance of the deviations of the true y's from their theoretical values. Thus, if the F-value is "large," the model is worthwhile, i.e., the regression is significant.

The multiple regression analysis estimates the regression coefficients (the α's) and thus produces a predicting equation. Since the estimates of the α's are functions of the data, the regression coefficients themselves have probability distributions. Any regression coefficient can be tested versus the null hypothesis $\alpha = 0$, and the test statistic for these tests in the t-value. If a regression coefficient has an insignificant t-value, then there is insufficient confidence that the α estimate has the proper sign and such an α is called insignificant.

The four quantitative variables X_1 = DDT feed rate (lb/hr), X_2 = primary chamber temperature (°C), X_2 = excess air (%), X_4 = retention time (sec) were used as the independent variables in two multiple regression analyses where the values Y_1 = relative amount of unburned DDT (%), and Y_2 = relative amount of unburned chlorinated hydrocarbon species, were the dependent variables. That is, a knowledge of DDT feed rate, primary chamber temperature, percent excess air, and retention time was used to predict Y_1 and Y_2, i.e., the efficiencies of DDT incineration.

In neither case was the regression significant, nor were any individual regression coefficients significant. Thus, knowing the values of feed rate, primary chamber temperature, percent excess air, and retention time does not materially aid one in predicting incineration efficiencies of DDT.

The results of these multiple regression analyses can be summarized as follows.

Y_1 = (DDT in off-gas)/(DDT fed)

Variable	Regression coefficient t-value	
X_1 = DDT rate	- 1.026	not significant
X_2 = primary chamber temp.	- 0.881	not significant
X_3 = excess air percent	0.526	not significant
X_4 = retention time	- 1.48	not significant

F-value for regression = 1.28 (not significant)

Y_2 = (Total chlorinated hydrocarbon species in off-gas)/(DDT fed)

X_1 = DDT rate	- 0.900	not significant
X_2 = primary chamber temp.	- 0.653	not significant
X_3 = excess air percent	0.498	not significant
X_4 = retention time	0.206	not significant

F-value for regression = 0.73 (not significant)

Two additional multiple regression models of the same form $Y_i = \alpha_0 + \alpha_1 X_{1i} + \ldots$ were estimated where:

$Y_i^{(1)} = i^{th}$ DDT content of off-gas (g/hr),

$Y_i^{(2)} = i^{th}$ total species content of off-gas (g/hr),

$X_{1i} = i^{th}$ DDT feed rate (lb/hr),

$X_{2i} = i^{th}$ primary chamber temperature (°F),

$X_{3i} = i^{th}$ excess air (%),

$X_{4i} = i^{th}$ primary chamber retention time (sec).

Another variable that is potentially influential is turbulence; turbulence exists only at "levels" 1 and 2. Therefore turbulence is not of a good form to include as an independent variable in a regression analysis, and the effects of turbulence on $Y^{(1)}$ and $Y^{(2)}$ were evaluated by the Mann-Whitney U test.

The original experimental design was a fractional factorial design, so the two levels of turbulence "see" virtually the same combination of the other independent variables. Thus the Mann-Whitney U test is a suitable technique with which to examine turbulence effects.

Neither the mean $Y^{(1)}$ nor the mean $Y^{(2)}$ was significantly affected by the turbulence level ($Z^{(1)} = 0.36$, $Z^{(2)} = 0.50$). However, the variance of $Y^{(1)}$ was affected by turbulence level ($Z = 2.35$, $\alpha < 0.05$); i.e., DDT content was more erratic at turbulence level 1 than at turbulence level 2. This influence does not apply to $Y^{(2)}$ (total species content).

For the response $Y^{(2)}$ (total chlorinated hydrocarbons species content) neither the regression as a whole nor any individual term was significant, i.e., the independent variables do not significantly influence the chlorinated hydrocarbons content of the incinerator off-gas.

For the DDT content $\left(Y^{(1)}\right)$, however, the regression was significant ($F(4,16) = 5.19$), i.e., using a knowledge of the X's does allow one to predict DDT content of the effluent gas more accurately. The only independent variable with a significant regression coefficient was X_1, the DDT feed rate (lb/hr). However, the α for X_3 (primary chamber temperature) was marginally significant ($\alpha < 0.10$).

Since X_2 and X_4 did not help, the multiple regression using only X_1 and X_3 was also computed. In this model, both terms are statistically significant. The precision of this model was found to be 98% as good as the model with all 4 X's.

Therefore we conclude that X_1 (DDT feed rate) and X_3 (primary chamber temperature) do significantly influence the DDT content of the off-gas. Specifically, the predictive equation is

$$Y^{(1)} = 0.285 + 0.0145\, X_1 - 0.00015\, X_3$$

where $Y^{(1)}$ = DDT content of off-gas (g/hr),

X_1 = DDT feed rate (lb/hr), and

X_3 = primary chamber temperature (°F).

Finally, one should point out that the ratio of precision in $Y^{(1)}$ when predicted by X_1 and X_3 to precision in $Y^{(1)}$ without knowledge of X_1 or X_3 is 75%. Thus 75% of the uncertainty in DDT content remains even after the influences of X_1 and X_3 are accounted for.

The DDT efficiencies determined from these experiments are not unlike those reported in an earlier study by the Defense Research Establishment of Canada. Their report showed that no more than 0.0002% of the DDT entering their incinerator remained unburned.[14/] These test results, reported to the same number of decimal points, indicate < 0.0005% DDT remained unburned (Experiments A and C, Table 25).

Upon completion of experiments with the 25% DDT EC formulation, eight tests were made using a 10%* dust formulation. These limited additional tests were made in order to evaluate the effect of physical form on the previously established efficiency of DDT combustion.

Turbulence was varied for the dust experiments by injecting the dust horizontally from two positions. For Configuration 1, both the dust injection nozzle and the fuel oil burner were located in the front burner position. The dust was injected horizontally at a 30-degree angle to the fuel oil burner. For Configuration 2, the oil burner was located in the front (primary) position, while the dust injection nozzle was located in the side (alternate) position (see Figure 2, p. 22). Thus, the burner flame and dust stream in Configuration 2 impinged at 90 degrees on a horizontal plane at the geometric center of the primary chamber.

Data from the eight 10% DDT dust experiments are summarized in Tables 28 through 32. The efficiency figures reported in the last two columns of Table 29 are based on the total unburned DDT and total species,** respectively, found in the effluent gas and the solid residue deposited on the walls and in the bottom of the incinerator, i.e., the content of the gas evolved during the 60-min sampling period, plus the appropriate fraction of the content of the total solid residue recovered from the system.

The possibility of emissions of dust-containing pesticide from the stack makes it necessary to determine the stack dust loading for accurate evaluation. Sampling the incinerator effluent using only the vapor sampling technique that was employed for liquid formulation would not reflect the pesticide content of dust emitted.

---

* Actual DDT content of the dust ranged from 5.5 to 6.3%.

** DDT plus all other chlorinated hydrocarbon species detected.

Table 28. SUMMARY OF 10% DDT DUST EXPERIMENTS

Run No.	No. 2 fuel oil rate		Pesticide feed rate		Turbulence[c]	Primary chamber temperature °C (°F)	Excess air[d] %	Retention time[e] sec		Sampling time min	Off-gas flow rate[f] m^3/hr (1,000's of SCFH)
	Nominal burner size ℓ/hr (gal/hr)	Actual rate ℓ/hr (gal/hr)	~ 10% Dust formulation kg/hr (lb/hr)	Contained DDT g/hr (lb/hr)[b]				Primary chamber	Second chamber		
A	13.2 (3.5)	NA[a]	17.14 (37.8)	1010 (2.22)	2	1210 (2210)	79	1.4	1.4	60	360 (12.7)
B	13.2 (3.5)	NA	16.19 (35.7)	950 (2.10)	1	1140 (2080)	58	1.9	2.0	60	263 (9.3)
C	13.2 (3.5)	NA	16.69 (36.8)	980 (2.16)	1	930 (1710)	164	1.4	1.2	60	462 (16.3)
D	11.3 (3.0)	9.73 (2.57)	16.10 (35.5)	1020 (2.24)	1	1030 (1880)	84	2.4	2.5	60	227 (8.0)
E	13.2 (3.5)	13.25 (3.50)	29.75 (65.6)	1720 (3.80)	1	1010 (1850)	128	1.3	1.2	60	422 (14.9)
F	11.3 (3.0)	9.88 (2.61)	37.91 (83.6)	2230 (4.91)	1	1120 (2050)	111	2.0	2.0	60	283 (10.0)
G	11.3 (3.0)	9.73 (2.57)	37.91 (83.6)	2230 (4.91)	1	1020 (1860)	156	1.6	1.6	60	362 (12.8)
H	11.3 (3.0)	10.48 (2.77)	17.10 (37.7)	1010 (2.22)	2	1030 (1880)	124	2.1	2.2	60	272 (9.6)

---

[a] Not determined.

[b] Actual DDT content of the ~ 10% dust formulation. Concentration of the DDT in this formulation ranged from 5.5 to 6.3%.

[c] 1 = Both fuel oil burner and dust nozzle in front burner position, at a 30-degree angle to one another.
2 = Fuel oil burner in front burner position and dust nozzle in side position at a 90-degree angle to one another.

[d] Calculated according to Method 3 of "Standards of Performance for New Stationary Sources," Federal Register, 36(247):24876-24895 (23 December 1971).

[e] Retention time is defined as $\frac{V}{v}$, where v is the wet off-gas flow rate from the incinerator at the respective chamber temperature and pressure, and V is the volume of that chamber.

[f] As dry gas at one atmosphere pressure, and 21.1°C (70°F).

Table 29. RESIDUE AND OFF-GAS CHARACTERISTICS--10% DDT DUST EXPERIMENTS

	Pesticide feed rate		Solid residues						Ratio of residues	
			Primary chamber			Second chamber				
Run No.	10% Dust formulation kg/hr (lb/hr)	Contained DDT[a] g/hr	Total kg/hr (lb/hr)	DDT conc. ppm	Total species[b] conc., ppm	Total kg/hr (lb/hr)	DDT conc. ppm	Total species[b] conc., ppm	Primary chamber to second chamber	Total residues to total dust fed
A	17.16 (37.8)	1,010	5.80 (12.8)	0.33	0.69	1.86 (4.1)	0.46	0.63	3.2	0.45
B	16.19 (35.7)	950	5.90 (13.0)	0.66	0.76	1.50 (3.3)	0.68	0.80	4.0	0.46
C	16.69 (36.8)	980	3.67 (8.1)	0.60	0.84	3.17 (7.0)	0.72	0.93	1.9	0.41
D	16.10 (35.5)	1,020	4.94 (10.9)	0.32	0.44	2.58 (5.7)	0.83	0.91	1.9	0.47
E	29.75 (65.6)	1,720	9.34 (20.6)	0.12	0.14	4.49 (9.9)	1.05	1.13	2.1	0.47
F	37.91 (83.6)	2,230	13.92 (30.7)	0.18	0.22	3.76 (8.3)	0.91	0.98	3.7	0.47
G	37.91 (83.6)	2,270	14.97 (33.0)	0.42	0.67	5.17 (11.4)	0.19	2.48	2.9	0.53
H	17.10 (37.7)	1,010	5.58 (12.3)	5.56	8.44	2.27 (5.0)	3.04	3.59	2.5	0.46

Run No.	DDT content of off-gas g/hr	DDT content of solid residues g/hr	Total DDT content of off-gas and solid residues g/hr	Total species[b] content of off-gas g/hr	Total species[b] content of solid residues g/hr	Total species[b] content of off-gas and solid residues g/hr	Ratio of DDT in off-gas to to total DDT fed	Ratio of total species[b] in off-gas to total DDT fed	Incineration efficiency[c] % DDT	Incineration efficiency[c] % Total species[b]
A	1.7×10^{-2}	4.1×10^{-3}	2.1×10^{-2}	2.3×10^{-2}	5×10^{-3}	2.8×10^{-2}	1.7×10^{-5}	2.3×10^{-5}	>99.99	> 99.99
B	6×10^{-2}	4.8×10^{-3}	6×10^{-2}	1.0×10^{-1}	6×10^{-3}	1.1×10^{-1}	6×10^{-5}	1.0×10^{-4}	>99.99	> 99.98
C	9×10^{-3}	4.5×10^{-3}	1.4×10^{-2}	1.7×10^{-2}	6×10^{-3}	2.3×10^{-2}	9×10^{-6}	1.7×10^{-5}	>99.99	> 99.99
D	8×10^{-3}	3.7×10^{-3}	1.1×10^{-2}	1.0×10^{-2}	4.6×10^{-3}	1.5×10^{-2}	7×10^{-6}	1.0×10^{-5}	>99.99	> 99.99
E	1.5×10^{-2}	6×10^{-3}	2.1×10^{-2}	1.8×10^{-2}	6×10^{-3}	2.5×10^{-2}	9×10^{-6}	1.0×10^{-5}	>99.99	> 99.99
F	2.0×10^{-2}	6×10^{-3}	2.6×10^{-2}	2.6×10^{-2}	7×10^{-3}	3.3×10^{-2}	9×10^{-6}	1.2×10^{-5}	>99.99	> 99.99
G	1.5×10^{-2}	1.6×10^{-2}	3.1×10^{-2}	2.0×10^{-2}	2.0×10^{-2}	4.0×10^{-2}	7×10^{-6}	9×10^{-6}	>99.99	> 99.99
H	1.2×10^{-2}	3.8×10^{-2}	5×10^{-2}	1.7×10^{-2}	6×10^{-2}	7×10^{-2}	1.2×10^{-5}	1.7×10^{-5}	>99.99	> 99.99

---

[a] Actual DDT content of the ~ 10% dust formulation.

[b] DDT plus all other chlorinated hydrocarbon species detected.

[c] Efficiency is defined as $\left[1 - \frac{\text{quantity out}}{\text{quantity in}}\right] \times 100$, where the quantity out is evaluated at Sample Points Nos. ② (the incinerator off-gas) and ③ (solid residues), and the quantity in is evaluated at Sample Point No. ① (the incinerator feed). Efficiencies have been calculated based on: (a) DDT only; and (b) the total chlorinated hydrocarbon species detected at Sample Points Nos. ② and ③.

Table 30. OFF-GAS COMPOSITION--10% DDT DUST INCINERATION[a]

			Total hydrocarbons analyzer			Orsat analyzer			
Run No.	DDT mg/m3	Total species[b] mg/m3	Total hydrocarbons ppm	CO ppm	CH_4 ppm	O_2 vol. %	CO_2 vol. %	CO vol. %	Moisture vol. %
A	4.7×10^{-2}	6.4×10^{-2}	NA[c]	NA	NA	9.5	8.6	0.0	6.6
B	2.2×10^{-1}	3.8×10^{-1}	NA	NA	NA	7.9	9.8	0.0	8.5
C	2.0×10^{-2}	3.7×10^{-2}	4	93	5	13.3	5.8	0.0	6.2
D	3.3×10^{-2}	4.4×10^{-2}	5	150	32	9.9	8.4	0.0	11.9
E	3.5×10^{-2}	4.3×10^{-2}	12	13	3	12.0	7.0	0.0	9.2
F	7.0×10^{-2}	9.2×10^{-2}	NA	NA	NA	11.2	7.6	0.0	7.6
G	4.1×10^{-2}	5.5×10^{-2}	NA	NA	NA	13.0	6.2	0.0	6.1
H	4.4×10^{-2}	6.3×10^{-2}	15	> 47[d]	26	12.1	6.6	0.0	6.7

---

[a] As dry gas at one atmosphere pressure, and 21.1°C (70°F).

[b] DDT plus all other chlorinated hydrocarbon species detected.

[c] No analysis.

[d] Analyzer attenuation setting too low.

Table 31. PARTICULATE SAMPLING SUMMARY--10% DDT DUST EXPERIMENTS

Description	A	B	C	D	E	F	G	H
Vol. dry-gas - std. cond., nm^3	0.511	0.413	0.757	0.427	0.733	0.474	0.624	0.490
Percent moisture by vol.	6.6	8.5	6.2	11.9	9.2	7.6	6.1	6.7
Avg. stack temperature, °C	468.5	385.2	480.3	343.8	493.5	381.5	369.2	360.4
Stk. flow rate, dry, std. cn., nm^3/min	6	4	8	4	7	5	6	5
Actual stack flow rate, m^3/min	16	11	21	9	20	11	14	10
Percent isokinetic	81.6	90.0	94.0	108.3	99.5	95.9	98.4	102.9
Percent excess air	76.7	58.4	165.1	83.1	127.9	111.8	158.6	129.2
Particulates - partial catch								
Particulate wt. - partial, mg	8,681	7,948	10,638	15,393	17,666	19,085	23,063	14,873
Part. load - ptl., std. cn., mg/nm^3	16,968	19,213	14,021	36,012	24,052	40,140	36,862	30,301
Part. load - ptl., stk. cn., mg/m^3	6,302	7,783	5,099	15,300	8,450	16,548	15,739	13,247
Partic. emis. - partial, kg/hr	6.10	5.06	6.49	8.14	10.18	11.41	13.34	8.23
Particulates - total catch								
Particulate wt. - total, mg	8,700	7,971	10,643	15,401	17,672	19,087	23,106	14,888
Part. load - ttl., std. cn., mg/nm^3	17,005	19,268	14,027	36,031	24,061	40,145	36,930	30,332
Part. load - ttl., std. cn. and 12% CO_2, mg/nm^3	23 700	23,600	29,000	51,000	41,000	63,000	71,000	55,000
Part. load - ttl., std. cn., mg/m^3	6,315	7,805	5,101	15,308	8,453	16,550	15,768	13,261
Partic. emis. - total, kg/hr	6.11	5.08	6.49	8.15	10.18	11.41	13.36	8.23
Percent impinger catch	0.21	0.29	0.04	0.05	0.03	0.01	0.18	0.10

Table 32. OPERATIONAL DATA SUMMARY--10% DDT DUST EXPERIMENTS

Run No.	A	B	C	D	E	F	G	H
Temperature °C (°F)								
Primary chamber (Thermocouple No. ①)	1180 (2160)	1090 (2000)	880 (1620)	990 (1820)	980 (1800)	1050 (1930)	940 (1730)	930 (1710)
Primary chamber (Thermocouple No. ②)	1210 (2210)	1100 (2020)	600 (1120)	1020 (1870)	860 (1580)	1070 (1950)	980 (1800)	920 (1690)
Primary chamber (Thermocouple No. ③)	1210 (2210)	1140 (2080)	930 (1710)	1030 (1880)	1010 (1850)	1120 (2050)	1020 (1860)	1030 (1880)
Second chamber (Thermocouple No. ④)	1060 (1940)	950 (1740)	860 (1580)	850 (1560)	920 (1680)	940 (1720)	870 (1600)	860 (1580)
Second chamber (Thermocouple No. ⑤)	730 (1340)	640 (1180)	700 (1290)	580 (1070)	740 (1360)	530 (980)	510 (950)	520 (960)
Sample Point No. ② (Thermocouple No. ⑥)	490 (920)	400 (760)	520 (960)	350 (670)	530 (930)	400 (760)	380 (720)	360 (680)
Pressures								
Draft (Manometer No. △), pascals (in. H_2O) gauge	39 (0.155)	22 (0.090)	52 (0.210)	12 (0.050)	46 (0.185)	32 (0.130)	42 (0.170)	19 (0.075)
Burner operation pressure, pascals (psi) gauge	NA[a]	7.4×10^5 (108)	7.4×10^5 (108)	7.7×10^5 (112)	NA[a]	7.4×10^5 (108)	7.5×10^5 (109)	7.5×10^5 (109)
Dust injection air, pascals (psi) gauge	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	9×10^4 (13)	1×10^5 (14)	1×10^5 (15)	6×10^4 (9)

---

[a] Pressure gauge broken.

It was therefore decided that the most accurate evaluation would be obtained by utilizing Method 5 of "Standard Performance for New Stationary Sources," as published in the Federal Register, 36(247):24876-24895, 23 December 1971, to determine the particulate loading in the stack. This technique, specified by EPA for use in such determinations, will give the total dust (particulate) discharged from the incinerator stack. The particulate sample, after collection, can then be analyzed for residual pesticide content.

Two modifications were made to facilitate the analysis of the sample for DDT content. First, pesticide grade benzene was used in the impingers rather than water. The second modification was to add a liquid nitrogen cold trap to the sample train in order to collect condensibles for DDT analysis. After particulate analysis had been completed, all samples were analyzed for DDT content (see Section IV and Appendix C of this report for a detailed description of the sampling method).

The total residual DDT was determined by the sum of: (a) the appropriate fraction of the DDT contained in the residue remaining in the incinerator, based on the ratio of sampling period to total pesticide injection period; (b) the pesticide content and particulate loading of the stack; and (c) the pesticide in the vapor form in the stack.

A summary of the particulate loading results obtained in the eight tests is shown in Table 31. Line 6 of this table reports the value for percent isokinetic. This value reflects the degree of isokinetic sampling that was maintained during the test. Method 5 requires, for compliance testing, maintaining percent isokinetic within 90 to 110. These limits were maintained during the tests in all except Run A. We can, therefore, state that we obtained a representative sample of the particulates in all but Run A. In Run A, since the value was less than 100%, the sampling velocity was less than isokinetic, and a larger fraction of the smaller particles was sampled. This would make the indicated particle loading value somewhat lower than the true value.

The other values of particular importance to the program are lines 14 and 16, Particle Load-Total at standard condition (dry gas at one atmosphere pressure, and 21.1°C (70°F)) and Particle Emission Total. The particle loading is reported in mg/m^3. This value, according to Title 40, CFR, (Part 60, Subpart 60.50), must not exceed 183 mg/m^3 on a new facility wity a capacity $\geq 4.5 \times 10^4$ kg/day (50 tons/day). This indicates that an incinerator, if required to meet federal regulations while combusting dust-pesticide formulation, would probably require emission control.

The particle emission-total reports emission in kg/hr. The measure is sometimes used in control regulations, but does not reflect the size of the operating unit. A small unit could have a relatively high particle density and still meet this type of emission criteria.

The only other data of direct importance are shown in the last line, Percent Impinger Catch. The impinger catch consists of particles which pass through the sample filter (less than 0.8 μ) and organic vapors collected in the impinger solvent. The impinger catch data for the 10% DDT dust experiment indicate that only a small fraction of the total discharge consists of organic volatiles and very fine particulates.

DISCUSSION

Significant corrosion was noted during the system cleanup, primarily in the first water scrubber (see Figure 1, p. 21). Both the conical reducer nozzle, (12 in.) diameter to (6 in.) diameter, and the demister pad (constructed of 304 stainless steel) had been almost entirely corroded out. Corrosion was also noted on the tank section of the first scrubber. Both the reducer nozzle and the tank section of this scrubber were replaced. Corrosion was also noted on the vertical piping leading down to the first water scrubber as well as to the two water nozzles in this section of pipe.

References

1. Lawless, E. W., R. von Rümker, and T. L. Ferguson, "The Pollution Potential in Pesticide Manufacturing," EPA Contract No. 68-01-0042 (June 1972).

2. von Rümker, R., and F. Horay, Pesticide Manual, Contract No. AID/csd 3296, Agency for International Development, U.S. Department of State (September 1972).

3. Zeidler, O., Ber., **7**:1180 (1874).

4. Wain, R. L., and A. E. Martin, Analyst, **72**:1 (1947).

5. Lord, K. A., J. Chem. Soc., 1657 (1948).

6. Fleck, E. E., Ind. Eng. Chem., **40**:706 (1948).

7. Beilstein's Handbuch der Organischen Chemie, 4th ed., E III 5, Syst. No. 479 (p. 1833), and Syst. No. 480 (p. 1981), Springer, Berlin.

8. Leigh, G., "Degradation of Selected Chlorinated Hydrocarbon Insecticides," J. WPCF, 41:R450 (1969).

9. Putnam, R. C., F. Ellison, R. Protzmann, and J. Hilovsky, "Organic Pesticides and Pesticide Containers--A Study of Their Decontamination and Combustion," Foster D. Small, Inc., Final Report on Contract No. CPE 69-140 (1971).

10. Whaley, H., G. K. Lee, R. K. Jeffrey, and E. R. Mitchell, "Thermal Destruction of DDT in an Oil Carrier," Can. Mines Br., Res. Rep., R225 (1970).

11. Montgomery, W. L., B. G. Cameron, and R. S. Weaver, "The Thermal Destructor," Report No. 270, Defence Research Establishment Suffield, Ralston, Alberta (Canada) (October 1971).

12. Lee, G. K., F. D. Friedrich, B. C. Post, and H. Whaley, "Thermal Destruction of DDT-Bearing Powders," Can. Mines Br., Res. Rep., R234 (1971).

13. Kennedy, M. V., B. J. Stojanovic, and F. L. Shuman, Jr., "Chemical and Thermal Methods for Disposal of Pesticides," Res. Rev., **29** 89 (1969).

14. Carnes, R. A., EPA/NERC-SHWRL, Personal communication to Mr. T. L. Ferguson (January 30, 1974).

II. ALDRIN

PESTICIDE DESCRIPTION

Physical Properties

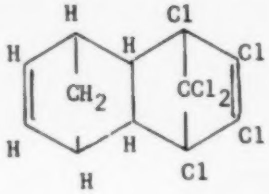
Chemical Name: 1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endoexo-5,6-dimethanonaphthalene; hexachlorohexahydro-endo,exo-dimethanonaphthalene; HHDN

Common Name: Aldrin (technical material containing not less than 95% of HHDN)

Trade Names: Aldrosol®, Aldrite®, Drinox®, Octalene®, Seedrin®

Pesticide Class: Broad spectrum insecticide; chlorinated hydrocarbon

Structural Formula:



Empirical Formula: $C_{12}H_8Cl$

Molecular Weight: 364.93

Physical State: Solid (at 25°C)

Solubility in:

Water at 20°C: 11 ppb

Organic Solvents: At 25°C moderately soluble in paraffins, aromatics, halogenated solvents, esters and ketones; sparingly soluble in alcohols.

Lipids, Fats: Soluble

Melting Point: Setting range 54 to 66°C (130 to 150°F)

Boiling Point: 34°C at 1 x 10^{-5} mm Hg

Vapor Pressure: 6 x 10^{-6} mm Hg at 25°C

Flammability: Not flammable

Stability: Slowly forms hydrochloric acid on storage and may, therefore, be corrosive to metal containers. Stable to heat, alkali and dilute acids; reacts with acid oxidizing agents, strong acids, phenols and active metals.

Chemical Properties

Aldrin is reported to be very stable thermally with no decomposition noted at 250°C.[1] Aldrin (along with the structurally related compounds dieldrin and isodrin) is stable to alkali (in contrast to chlordane and heptachlor)[2] and refluxing with aqueous or alcoholic caustic has no effect.[1]

Incineration has been recommended by the MCA Manual[3] for aldrin disposal. Putnam et al.[4] found that combustion of aldrin in polyethylene on a small scale gave more than 99% decomposition. Differential scanning calorimetry (DSC) analysis of aldrin by Putnam et al. indicated minor decomposition (based on exothermic peaks) over the range of 343 to 354°C and major decomposition from 383 to 403°C in a closed system (i.e., a sealed sample). In an open system, very small evidence of exothermic decomposition was detected over the range of 293 to 297°C.

Production and Use

Aldrin has been one of the most widely used soil insecticides. However, its use is currently the subject of litigation, and aldrin is not currently being produced in the United States. Estimated 1972 domestic production of aldrin was 13 million pounds (von Rümker et al.[5]).

Commercial formulations that have been available include: emulsifiable concentrates (44.2% = 4 lb/gal); wettable powder (25%), granules (20%), dusts and dust concentrates, seed dressings, fertilizer mixtures, and oil solutions.

FORMULATIONS TESTED

Two aldrin formulations were tested, a 4 lb/gal EC, and a 20% granule.

4 lb/gal EC

Name: Shell Aldrite® 4

Manufacturer: Shell Chemical Company, Agricultural Chemicals Division, New York, New York

Composition:

Active ingredient (by weight)	
Aldrin	43.4%*
Petroleum hydrocarbons	50.6%
Inert ingredients (by weight)	6.0%
Total	100.0%

---

* Equivalent to 41.2% aldrin plus 2.2% related compounds.

Registration: EPA Reg. No. 201-245-AA

Lot No.: 3-RCA-4306, 3-RCA-4319

20% Granules

Name: Shell Aldrin 20G

Manufacturer: Shell Chemical Company, Agricultural Chemicals Division, New York, New York

Composition:

Active ingredient (by weight)	
Aldrin	20.0%*
Inert ingredients	80.0%
Total	100.0%

---

* Equivalent to 19.0% aldrin and 1.0% related compounds.

Registration: EPA Reg. No. 202-214-AA

Lot No.: H332804, H332805, H332807, and 52-1262

Particle Size Specification: Formulated on 20/40 attapulgite clay (smaller than 841 μ, larger than 420 μ in size)

PRELIMINARY THERMAL ANALYSIS

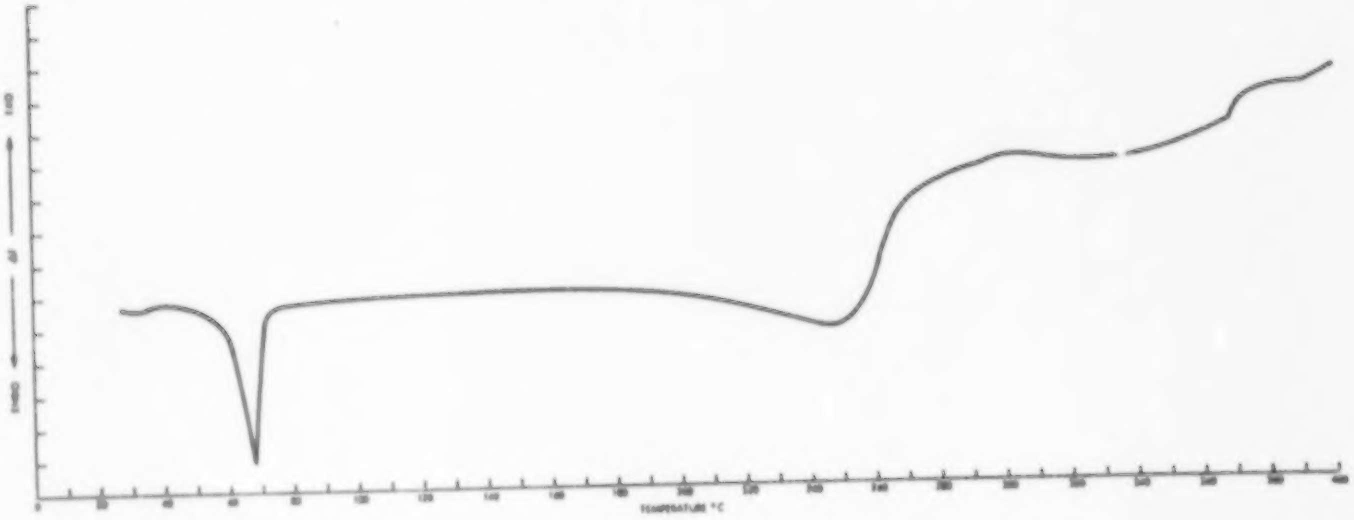
Bomb calorimetric analyses of aldrin gave the following results:

Sample	Test	Test method	Result
41.2% Aldrin Emulsifiable Concentrate	Heat of combustion	ASTM D-240	3.098×10^7 J/kg (13,331 Btu/lb)
	Sulfur	ASTM C-129	0.38%
19.0% Aldrin (granular)	Calorific value	ASTM D-2015	5.708×10^6 J/kg (2,456 Btu/lb) (no sulfur correction)
Aldrin (technical grade)	Calorific value	ASTM D-2015	1.786×10^7 J/kg (7,684 Btu/lb)
	Sulfur	ASTM D-129	0.70%

DTA and TGA were run using a Du Pont Model 900 differential thermal analyzer, and a Perkin-Elmer Model TGS-1 Thermobalance (equipped with Perkin-Elmer temperature program control UU1), respectively.

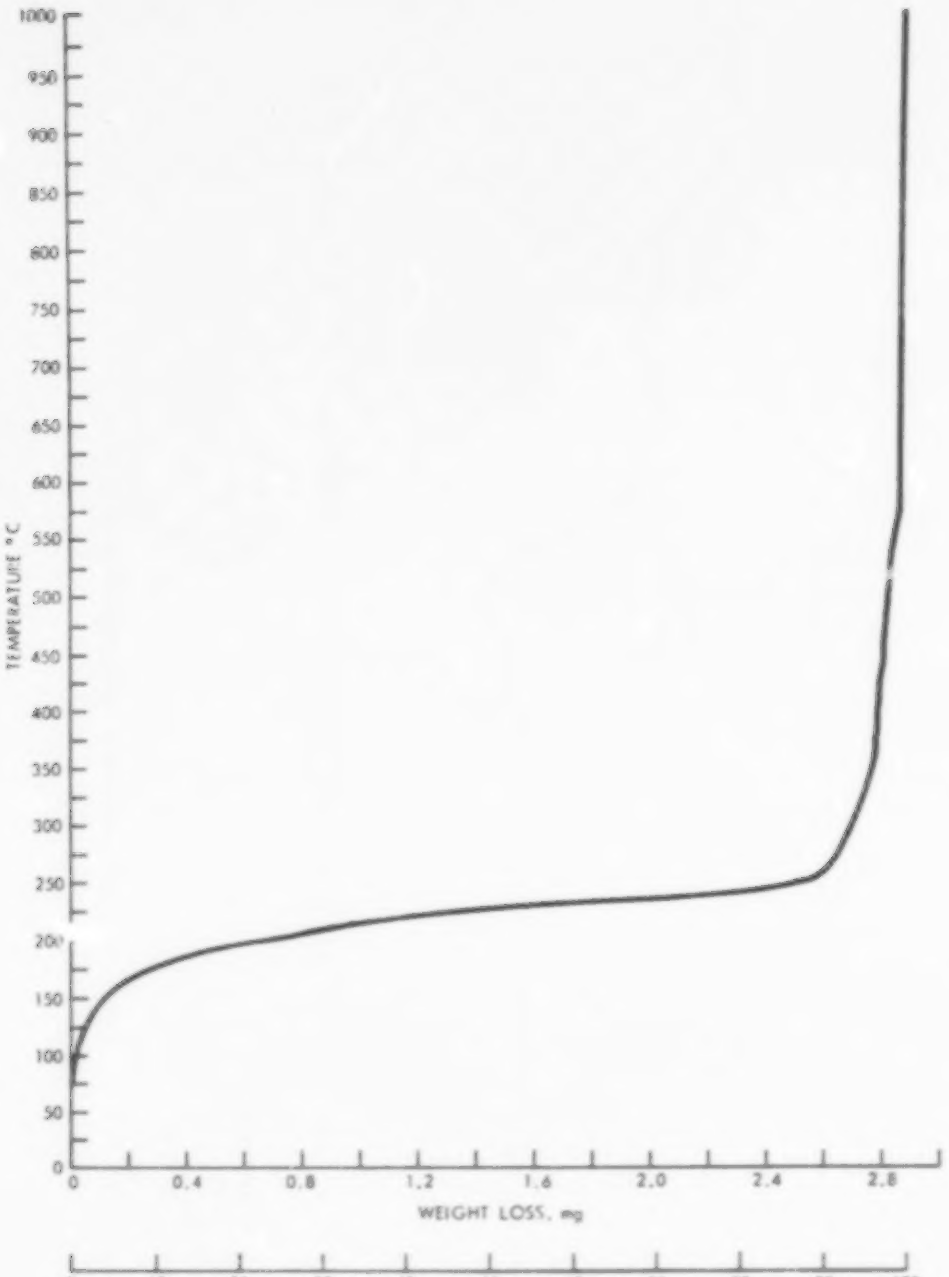
Figures 21 and 22 show the results of DTA and TGA of a sample of recrystallized aldrin obtained by evaporation of a sample of the EC formulation. The DTA data (Figure 21) on aldrin show two endotherms, one at 60 to 66°C, and the other at 210 to 250°C. The first endotherm indicates a phase change (TGA data in Figure 22 show no significant weight loss at 60 to 70°C). The latter endotherm could very well be the vaporization of the liquid. Significant weight loss is observed at this temperature on the TGA data. Beyond 250°C, however, an exothermic process is observed which indicates that the sample is undergoing decomposition. This is substantiated by TGA which shows continued weight loss up to about 570°C. At this temperature, virtually no sample remained.

DTA and TGA analyses of the ~ 19% granular formulation of aldrin are shown in Figures 23 and 24. The DTA data show that there are two decomposition processes--one at ~ 175°C and the other at ~ 370°C. This is substantiated by the TGA which shows continuous weight loss as temperature increases (Figure 24). At about 270°C almost 25% of the original weight is gone, which corresponds to the nominal 20% aldrin content of the formulation. As the heating of the formulation continues to 700°C, another 10% is lost. From 700 to 1000°C there is essentially no weight loss recorded. Thus, it is probable that the aldrin in this formulation would be destroyed at 700°C.



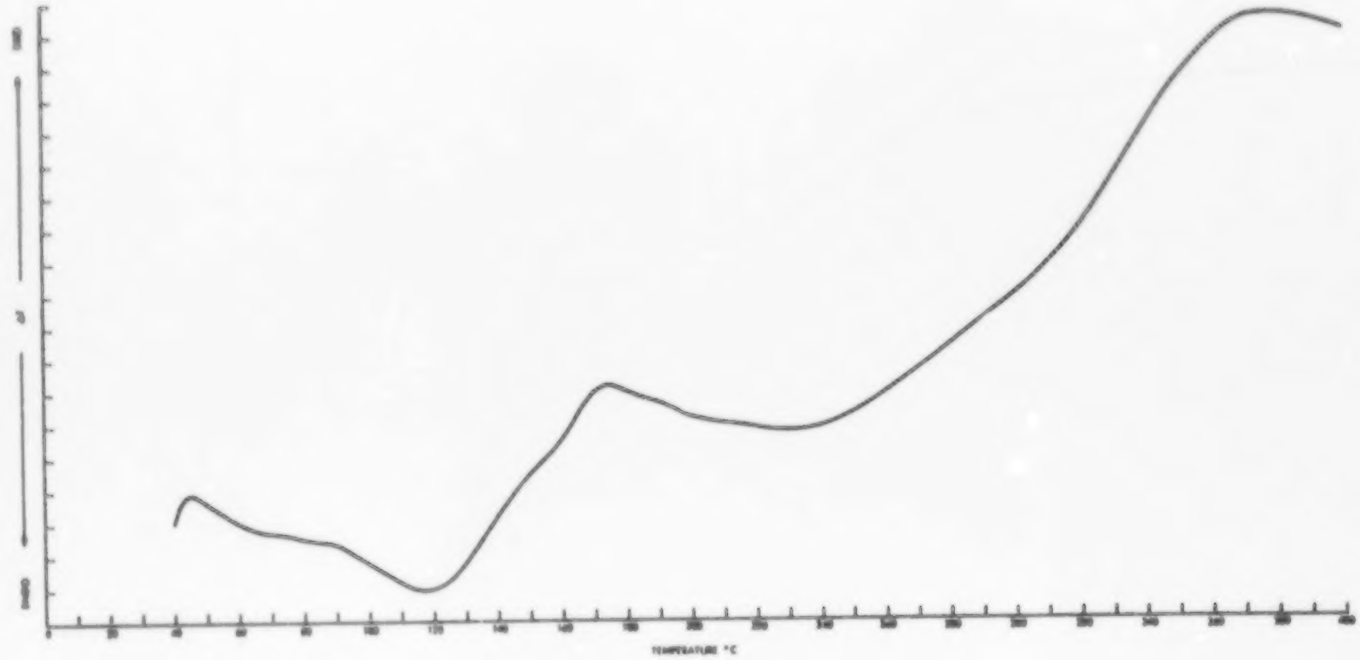
Reference: Glass beads
Prog. mode: Heat
Rate: 10°C/min
Start: 28°C

Figure 21. DTA analysis of recrystallized aldrin



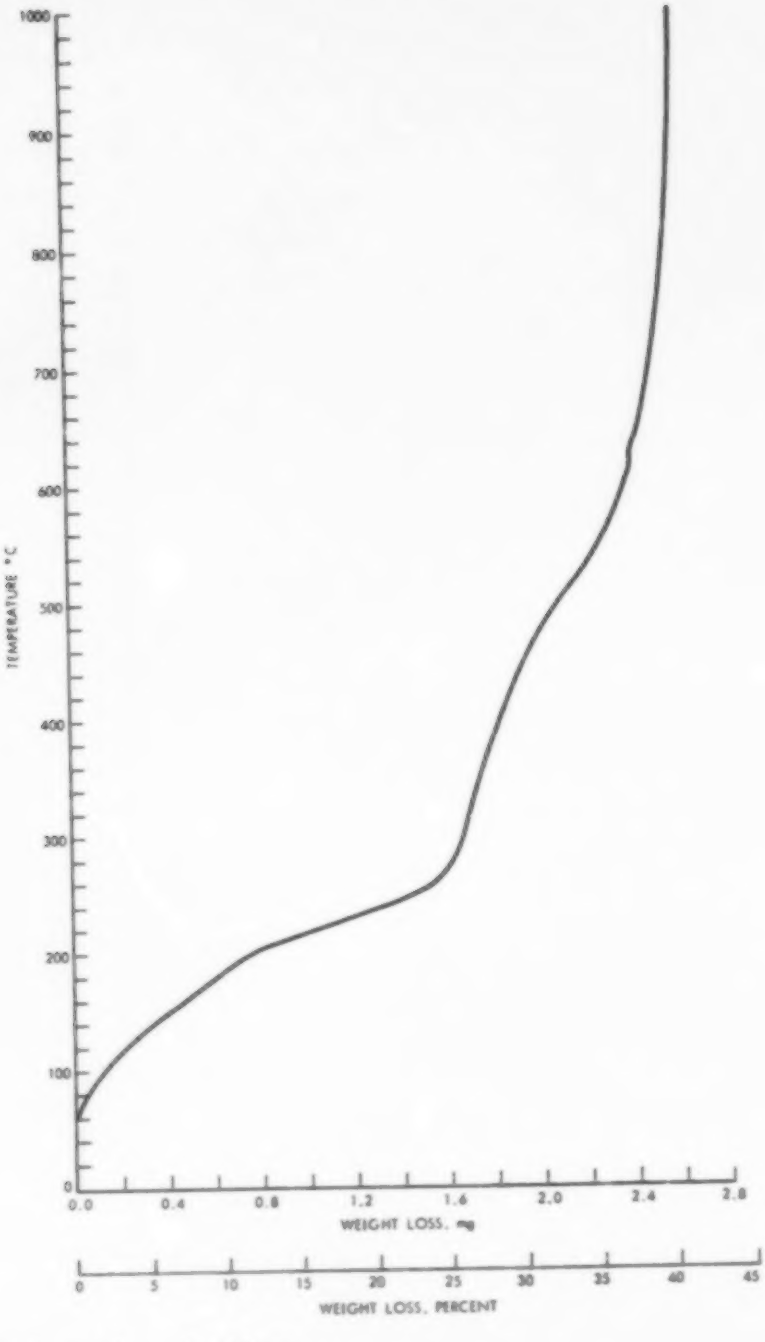
Heating rate: 20°C/min
Environment: ~ 20 ml/min air (20% O_2, 80% N_2)

Figure 22. TGA analysis of recrystallized aldrin



Reference: Glass beads
Prog. mode: Heat
Rate: 10°C/min
Start: 40°C

Figure 23. DTA analysis of 19% aldrin granules



Sample weight: 6.422 mg
Heating rate: 20°C/min
Environment: ~ 20 ml/min air (20% O_2, 80% N_2)

Figure 24. TGA analysis of 19% aldrin granules

METHODS OF ANALYSIS

Apparatus

A Micro-Tek 2000 R gas chromatograph equipped with a 3-ft, 4 mm I.D. glass column (packed with 1.5% OV-17 + 1.95% QF-1 on 80/100 mesh Supelcoport from Supelco, Inc., Bellefonte, Pennsylvania) and a tritium electron capture detector, maintained at a voltage of 15 V DC, were used for gas chromatographic analysis. Chromatographic operating conditions were: injector temperatue, 190°C; column temperature, 175°C; detector temperature, 180°C; carrier flow rate, 80 ml/min, N_2; and purge gas flow rate, 200 ml/min, N_2.

A Varian G-2000 strip chart recorder was used to record the chromatograms.

Reagents and Materials

The solid standard, aldrin (97% pure) used to prepare standard solutions. Solvents used were pesticide grade 2,2,4-trimethylpentane (Matheson, Coleman, Bell) for solution of standards and extraction of all water-based samples and pesticide grade hexane (Matheson, Coleman, Bell) for extraction of hexylene glycol traps from the second stage scrubber. All laboratory glassware was washed in Alconox detergent (Scientific Products) and rinsed in deionized distilled water and reagent grade acetone (Fisher Scientific).

Standards and Calibration Curves

The solid aldrin standard was used to prepare a stock solution of 100 μg/ml and appropriate dilutions were made to produce a linear curve (linear range used: 0 to 10 pg).

Procedure for Sample Preparation

All samples collected in water from the liquid aldrin formulation tests were extracted with two 5-ml portions of 2,2,4-trimethylpentane. Twenty milliliters of the hexylene glycol samples (from the second stage scrubber) were extracted with two 5-ml portions of hexane. Appropriate amounts (1 to 5 μl) of these extracted samples and the samples collected in 2,2,4-trimethylpentane were injected into the gas chromatograph.

The mass of collected particulates was determined for all samples from incineration of granular aldrin tests as follows. Samples were taken to dryness in clean, dessicated, tared 250-ml beakers and dessicated 2 days before final weighing. The residues were extracted with 2,2,4-trimethylpentane (10 or 20 ml depending on amount of residue) and appropriate portions of these extracts were injected for GC analysis.

Blank impinger samples were analyzed directly as they came from the field. The silica gel was extracted with enough 2,2,4-trimethylpentane to cover the silica gel and a portion analyzed by gas chromatography.

Portions of all solid residues (primary chamber, secondary chamber, etc.) were weighed out, extracted, and the extracts analyzed for aldrin.

Analysis and Discussion

A chromatogram of the liquid aldrin formulation diluted to 5 x 10^5 times in 2,2,4-trimethylpentane showed a total of nine peaks (see Figure 25). Peaks 7 and 9 are identified as aldrin and dieldrin, respectively, based on relative retention time of standards. Peaks 5, 6, and 8 were at first thought to be lindane, heptachlor, and heptachlor epoxide, respectively. However, comparison with the relative retention time of the standards showed differences of 0.1 min for lindane, 0.1 min for heptachlor, and 0.5 min for heptachlor epoxide. All of these unidentifiable peaks were termed as unknowns, and their respective concentration present in each sample collected from the incinerator system for analyses was calculated based on the aldrin calibration curve.

The sensitivity of the instrument for aldrin is 1 pg. Based on this sensitivity, and with a 5 μl sample injection for each analysis, the minimum detectable value for a 20-ml sample solution is 4 ng. However, during the analysis samples were very often concentrated to 1 ml, giving a minimum detectable value of < 1 ng.

TEST CONDITIONS AND RESULTS

The experimentation with aldrin, and for all other pesticides subsequently studied, involved two phases. First, laboratory studies were made to determine potentially favorable combustion conditions for each pesticide. Experiments were then conducted in the pilot-scale incinerator to verify the efficiency of combustion in the range of potentially favorable operating conditions.

For each pesticide studied, representative formulations and technical grade material were obtained. These materials were analyzed by differential thermal analysis, thermal gravimetric analysis, and bomb

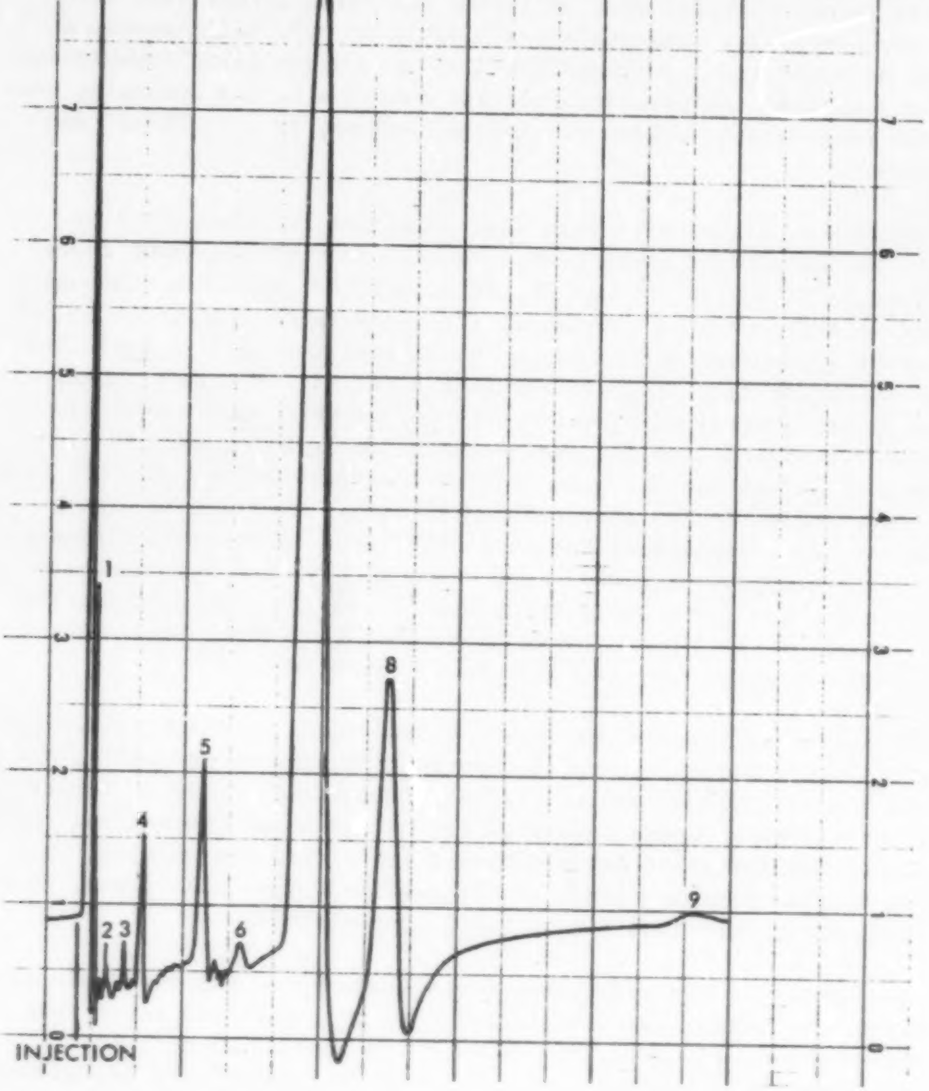


Figure 25. Chromatogram of 41.2% aldrin EC formulation

calorimetry. These thermal analyses were used to determine the temperature range at which the respective pesticide could be expected to decompose.

Following this definition, at least eight experiments utilizing a liquid formulation and four utilizing the solid formulation were made. For pesticides commercially available in only solid forms, a minimum of eight tests were conducted using a major solid formulation. Rate of pesticide incineration, percent excess air, and operating temperature were varied between two nominal values, i.e., a "high" and "low" level.

Initially, eight tests were made using the EC formulation of aldrin. The results of these tests (as well as two subsequent tests) are given in Tables 33 through 36. Efficiency of combustion was again defined in terms of a mass balance, i.e., aldrin charged into the system versus aldrin not destroyed in the incinerator (aldrin out). Reference to Figure 5, p. 27, will make this definition more evident. Aldrin in was determined by volumetric measurement and GC analysis of the mixture charged into the incinerator (Sample Point No. ①). Representative gas samples were collected at Sample Point No. ② (the undiluted, cooled incinerator effluent), and in combination with a volumetric determination of the total undiluted incinerator effluent, yielded the quantity of aldrin (and other chlorinated hydrocarbons) out. No solid residue (Sample Point No. ③ was generated during the incineration of the liquid formulation, and, therefore, Sample Point No. ③ did not enter into the efficiency calculation.

The efficiencies for the eight initial tests were all > 99.99%, based on either aldrin, or total chlorinated hydrocarbon species detected. However, all of the initial eight tests were made at temperatures significantly above those indicated (by differential thermal and thermal gravimetric analyses) as being required for aldrin degradation. This was due to the operating limit of the available fuel oil burner, which was designed to burn from 3.0 to 8.0 gal/hr of fuel.

Subsequently, two additional tests (Nos. 9 and 10) were made using a new fuel oil burner capable of operating at lower feed rates than the burner previously used. The lower rates enabled us to conduct these two additional runs at much lower temperatures. Runs 9 and 10, although conducted at primary chamber temperatures 440 to 500°C (800 to 900°F) lower than the initial eight runs also showed an efficiency of aldrin incineration of > 99.99%, based on aldrin or the total chlorinated species detected.

Table 33. SUMMARY OF 41.2% ALDRIN EC EXPERIMENTS

Run No.	Incinerator feed rate: Nominal burner size ℓ/hr (gal/hr)	Incinerator feed rate: Total feed rate ℓ/hr (gal/hr)	Incinerator feed rate: Aldrin rate g/hr (lb/hr)[a]	Incinerator feed rate: Aldrin rate ℓ/hr (gal/hr)[b]	Incinerator feed rate: No. 2 fuel oil rate ℓ/hr (gal/hr)	Primary chamber temperature °C (°F)	Flame temperature[c] °C (°F)	Excess air[d] %	Retention time[e] sec: Primary chamber	Retention time[e] sec: Second chamber	Sampling time min	Off-gas flow rate[f] m³/hr (1,000's of SCFH)
1	13.2 (3.5)	12.64 (3.34)	2,310 (5.09)	5.07 (1.34)	7.57 (2.00)	940 (1730)		209	2.5	2.3	30	229 (8.1)
2	15.1 (4.0)	18.70 (4.94)	3,480 (7.67)	7.65 (2.02)	11.05 (2.92)	1020 (1870)		128	1.9	1.6	30	283 (10.0)
3	15.1 (4.0)	14.57 (3.85)	2,470 (5.44)	5.41 (1.43)	9.16 (2.42)	1020 (1870)		164	2.0	1.9	30	252 (8.9)
4	7.6 (2.0)	5.22 (1.38)	1,610 (3.56)	3.56 (0.94)	1.66 (0.44)	920 (1690)		230	4.8	5.1	30	119 (4.2)
5	5.7 (1.5)	5.49 (1.45)	1,650 (3.63)	3.63 (0.96)	1.86 (0.49)	830 (1530)		203	4.3	4.6	30	156 (5.5)
6	5.7 (1.5)	5.07 (1.34)	660 (1.45)	1.44 (0.38)	3.63 (0.96)	850 (1560)	1380 (2510)	158	4.2	4.5	30	199 (5.8)
7	15.1 (4.0)	13.78 (3.64)	2,260 (4.98)	4.96 (1.31)	8.82 (2.33)	1050 (1920)	1400 (2550)	169	1.2	1.2	30	450 (15.9)
8	13.2 (3.5)	11.77 (3.11)	1,350 (2.98)	2.95 (0.78)	8.82 (2.33)	1140 (2080)	1440 (2630)	70	2.2	2.2	30	224 (7.9)
9	3.8 (1.0)	3.48 (0.92)	1,010 (2.23)	3.48 (0.92)	0	680 (1250)		332	4.8	5.3	30	153 (5.4)
10	2.8 (0.75)	2.69 (0.71)	620 (1.36)	2.69 (0.71)	0	600 (1120)	1100 (2020)	380	6.9	7.6	30	113 (4.0)

---

[a] Actual aldrin content of the incinerator feed.

[b] Volume of ~ 41.2% aldrin EC formulation in the fuel oil-pesticide mixture.

[c] Flame temperature was observed at a point approximately 15 cm (6 in.) in from the front wall of the incinerator (see Figure B-1).

[d] Calculated according to Method 3 of "Standards of Performance for New Stationary Sources," *Federal Register*, 36(247):24876-24895 (23 December 1971).

[e] Retention time is defined as $\frac{V}{v}$, where v is the wet off-gas flow rate from the incinerator at the respective chamber temperature and pressure, and V is the volume of that chamber.

[f] As dry gas at one atmosphere pressure and 21.1°C (70°F).

Table 34. INCINERATION EFFICIENCY--41.2% ALDRIN EC FORMULATION

Run No.	Aldrin feed rate[a] g/hr	Aldrin content of off-gas g/hr	Ratio of aldrin content of off-gas to aldrin fed	Total species[b] content of off-gas g/hr	Ratio of total species[b] content of off-gas to aldrin fed	Incineration efficiency[c] % Aldrin	Incineration efficiency[c] % Total species[b]
1	2,310	2.8×10^{-4}	1.2×10^{-7}	1.3×10^{-2}	6×10^{-6}	> 99.99	> 99.99
2	3,480	5×10^{-4}	1.5×10^{-7}	3.1×10^{-2}	9×10^{-6}	> 99.99	> 99.99
3	2,470	6×10^{-4}	2.4×10^{-7}	1.1×10^{-2}	4.4×10^{-6}	> 99.99	> 99.99
4	1,610	4×10^{-4}	2×10^{-7}	4×10^{-3}	3×10^{-6}	> 99.99	> 99.99
5	1,650	3×10^{-4}	2×10^{-7}	9×10^{-3}	5×10^{-6}	> 99.99	> 99.99
6	660	2×10^{-4}	3×10^{-7}	2×10^{-3}	3×10^{-6}	> 99.99	> 99.99
7	2,260	2.4×10^{-4}	1.1×10^{-7}	8×10^{-3}	3×10^{-6}	> 99.99	> 99.99
8	1,350	2.3×10^{-4}	1.7×10^{-7}	3.5×10^{-3}	2.6×10^{-6}	> 99.99	> 99.99
9	1,010	1×10^{-3}	1×10^{-6}	3×10^{-2}	3×10^{-5}	> 99.99	> 99.99
10	620	4×10^{-4}	6×10^{-7}	1×10^{-2}	2×10^{-5}	> 99.99	> 99.99

---

[a] Actual aldrin content of the incinerator feed.

[b] Aldrin plus all other chlorinated hydrocarbon species detected.

[c] Efficiency is defined as $\left[1 - \frac{\text{quantity out}}{\text{quantity in}}\right] \times 100$, where the quantity out is evaluated as Sample Point No. ② (the effluent gas), and the quantity in is evaluated at Sample Point No. ① (the incinerator feed). Efficiencies have been calculated based on (a) aldrin only, and (b) the total chlorinated hydrocarbon species detected at Sample Point No. ② .

Table 35. OFF-GAS COMPOSITION--41.2% ALDRIN EC INCINERATION[a]

					Total hydrocarbons analyzer			Orsat analyzer			
Run No.	Aldrin mg/m^3	Total species[b] mg/m^3	SO_2 mg/m^3	NO_x[d] mg/m^3	Total hydrocarbons ppm	CO ppm	CH_4 ppm	O_2 vol. %	CO_2 vol. %	CO vol. %	Mositure vol. %
1	1.2×10^{-3}	5.5×10^{-2}	17	69	9	6	> 8[e]	14.4	4.9	0.0	6.7
2	1.8×10^{-3}	1.1×10^{-1}	83	ND[c]	9	32	2	12.0	6.7	0.0	12.3
3	2.4×10^{-3}	4.5×10^{-2}	140	52	13	8	2	12.7	6.4	0.0	12.4
4	3.1×10^{-3}	3.7×10^{-2}	50	64	9	12	1	14.7	5.1	0.0	9.6
5	2.0×10^{-3}	5.5×10^{-2}	95	260	10	47	3	14.1	5.9	0.0	3.5
6	1.1×10^{-3}	1.3×10^{-2}	100	140	4	28	2	13.1	6.2	0.0	3.5
7	5.2×10^{-4}	1.7×10^{-2}	94	ND	9	25	2	12.8	6.2	0.0	4.9
8	1.0×10^{-3}	1.6×10^{-2}	190	ND	9	11	3	8.9	9.6	0.0	7.7
9	9.0×10^{-3}	1.8×10^{-1}	27	ND	35	204	9	16.3	3.7	0.0	5.6
10	3.2×10^{-3}	1.1×10^{-1}	ND[c]	ND	52	1,670	6	16.5	4.6	0.0	7.0

---

[a] As dry gas at one atmosphere pressure, and 21.1°C (70°F).

[b] Aldrin plus all other chlorinated hydrocarbon species detected.

[c] Not detected.

[d] Calculated as NO_2.

[e] Analyzer attenuation setting too low.

Table 36. OPERATIONAL DATA SUMMARY--41.2% ALDRIN EC EXPERIMENT

Run No.	1	2	3	4	5	6	7	8	9	10
Temperature °C (°F)										
Primary chamber (Thermocouple No. ①)	920 (1680)	990 (1810)	980 (1800)	900 (1650)	820 (1500)	830 (1520)	1050 (1920)	1120 (2040)	680 (1250)	600 (1120)
Primary chamber (Thermocouple No. ②)	840 (1540)	760 (1400)	930 (1700)	900 (1660)	800 (1480)	820 (1500)	1020 (1860)	1090 (1990)	620 (1140)	540 (1000)
Primary chamber (Thermocouple No. ③)	960 (1730)	1020 (1870)	1020 (1870)	920 (1690)	830 (1530)	850 (1560)	1050 (1920)	1140 (2080)	670 (1230)	600 (1110)
Second chamber (Thermocouple No. ④)	900 (1650)	990 (1820)	970 (1780)	790 (1460)	690 (1280)	710 (1310)	970 (1780)	960 (1760)	540 (1000)	480 (890)
Second chamber (Thermocouple No. ⑤)	640 (1190)	840 (1550)	660 (1220)	440 (830)	390 (740)	400 (750)	660 (1220)	680 (1260)	260 (500)	230 (450)
Sample Point No. ② (Thermocouple No. ⑥)	480 (900)	600 (1120)	530 (990)	270 (520)	250 (480)	260 (500)	540 (1000)	400 (760)	170 (330)	160 (320)
Pressures										
Draft (Manometer No. △1), pascals (in H_2O) gauge	45 (0.180)	50 (0.200)	41 (0.165)	12 (0.050)	14 (0.055)	14 (0.055)	47 (0.190)	12 (0.050)	17 (0.070)	16 (0.065)
Burner operation pressure, pascals (psi) gauge	7.6×10^5 (110)	7.4×10^5 (108)	7.4×10^5 (108)	7.6×10^5 (111)	8.1×10^5 (118)	8.1×10^5 (118)	8.0×10^5 (116)	8.0×10^5 (116)	NA[f]	NA
Scrubber liquids[a]										
1st Stage, H_2O scrubber										
Volume, ℓ (gal.)	1200 (318)	950 (250)	1070 (284)	1050 (277)	890 (234)	940 (248)	1080 (286)	920 (243)	1150 (304)	1090 (289)
Aldrin conc., mg/ℓ	ND[c]	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total species conc.,[b] mg/ℓ	1×10^{-3}	ND	ND	2×10^{-3}	1×10^{-3}	ND	2×10^{-3}	ND	3×10^{-3}	2×10^{-3}
2nd Stage, Hexalene glycol scrubber										
Volume, ℓ (gal.)	108 (28.6)	114 (30.1)	114 (30.1)	108 (28.6)	100 (26.4)	97 (25.6)	103 (27.1)	99 (26.1)	94 (24.8)	91 (24.1)
Aldrin conc. change, mg/ℓ	ND[d]	ND[d]	1×10^{-3}	ND[d]	2×10^{-3}	1×10^{-3}	1×10^{-3}	ND[d]	1×10^{-3}	1×10^{-3}
Total species conc. change,[b] mg/ℓ	1.1×10^{-4}	7×10^{-3}	8×10^{-3}	2×10^{-3}	2.2×10^{-2}	1×10^{-3}	2.1×10^{-2}	1.0×10^{-2}	3×10^{-3}	1×10^{-3}
3rd Stage, H_2O scrubber										
Volume, ℓ (gal.)	1850 (490)	1950 (515)	1950 (515)	1890 (500)	1760 (465)	1780 (470)	2020 (535)	1740 (460)	1890 (500)	1780 (470)
Aldrin conc., mg/ℓ	ND[c]	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total species conc.,[b] mg/ℓ	ND	ND	ND	ND	ND	1×10^{-3}	ND	1×10^{-3}	ND	ND
Scrubber system										
Effluent gas (Sample Point No. ⑨)[e]										
Aldrin conc., mg/m^3	1×10^{-3}	ND	2×10^{-3}	2×10^{-3}	ND	ND	ND	ND	8×10^{-4}	2×10^{-3}
Total species conc.,[b] mg/m^3	3×10^{-3}	1×10^{-2}	2×10^{-2}	6×10^{-3}	2×10^{-3}	2×10^{-3}	6×10^{-3}	2×10^{-2}	3×10^{-3}	1×10^{-2}

---

[a] Scrubber water (Scrubbers 1 and 3) was used once through, while the hexylene glycol (Scrubber 2) was recycled. The concentrations reported for hexylene glycol, therefore, are the concentration changes (increases) detected during the respective tests.

[b] Aldrin plus all other chlorinated hydrocarbons species detected.

[c] Not detected.

[d] No increases in concentration detected.

[e] As wet gas at one atmosphere pressure, and 21.1°C (70°F).

[f] Pressure gauge broken.

The relative amount of chlorinated species generated during Runs Nos. 9 and 10 (as shown by the "Ratio of Total Species Content of Off-Gas to Aldrin Fed" column in Table 34) was significantly higher than that for the tests conducted at higher temperatures. The relative aldrin content of the off-gas was also somewhat higher in the last two tests (see Table 34). Thus, it appears that incineration of aldrin at ~ 650°C (1200°F) is virtually as efficient as incineration at ~ 1090°C (2000°F) in terms of actual aldrin content, but is less efficient in terms of total chlorinated hydrocarbons detected in the incinerator effluent.

A granular formulation of aldrin was used to evaluate the effect of physical form on the efficiency of aldrin incineration.

The operation and analytical results for the six granule runs are summarized in Tables 37 through 41. All efficiencies of aldrin incineration are > 99.99%. The relatively high level of aldrin recovered at Sample Point No. ② on Run No. B, however, is suspect. Total pesticide recovery from the sample train at Sample Point No. ② is determined by summing that found in the probe cyclone, the filter element, the impinger contents, the impinger rinses, and the cold trap. While the levels of aldrin found in all other elements of the sample train were of normal magnitude, the aldrin level on the filter element for Run No. B was quite high, i.e., 162 times the next highest filter concentration. Thus, it is highly probable that the filter element was contaminated.

Method 5, as published in the Federal Register,[7/] was used to determine the particulate loading in the stack at Sampling Point No. ② (see Figure 5, p. 27). Two modifications were made to facilitate the analysis of the sample for aldrin content. First, pesticide grade 2,2,4-trimethylpentane was used in the impingers rather than water. The second modification was to add a liquid nitrogen cold trap to the sample train in order to collect condensibles for aldrin analysis. After particulate analysis had been completed, all samples were analyzed for aldrin content.

The total residual aldrin was determined by the sum of: (a) the appropriate fraction of the aldrin contained in the residue remaining in the incinerator, based on the ratio of sampling period to total pesticide injection period; (b) the pesticide content and particulate loading of the stack; and (c) the aldrin in the vapor form in the stack.

Table 37. SUMMARY OF 19% ALDRIN GRANULE EXPERIMENTS

	No. 2 Fuel oil rate		Pesticide feed rate					Retention time[d/] sec			
Run No.	Nominal burner size ℓ/hr (gal/hr)	Actual rate ℓ/hr (gal/hr)	~ 19% Granule formulation kg/hr (lb/hr)	Contained aldrin[a/] g/hr (lb/hr)	Primary chamber temperature °C (°F)	Flame temperature[b/] °C (°F)	Excess air %	Primary chamber	Second chamber	Sampling time min	Off-gas flow rate m^3/hr (1,000's of SCFH)[e/]
A	13.2 (3.5)	12.15 (3.21)	9.98 (22.0)	1,860 (4.09)	1150 (2100)	-	48	2.5	2.7	60	210 (7.4)
B	7.6 (2.0)	9.20 (2.43)	9.12 (20.1)	1,693 (3.73)	980 (1800)	-	155	2.7	2.6	60	266 (9.4)
C	5.7 (1.5)	5.83 (1.54)	19.55 (43.1)	3,630 (8.01)	890 (1630)	-	81	3.2	3.6	60	198 (7.0)
D	9.5 (2.5)	9.42 (2.49)	20.09 (44.3)	3,760 (8.26)	1030 (1890)	-	120	2.0	2.2	60	278 (9.8)
E	11.3 (3.0)	11.81 (3.12)	19.50 (43.0)	3,630 (8.00)	1100 (2020)	1280 (2330)	118	1.4	1.4	60	377 (13.3)
F	5.7 (1.5)	5.83 (1.54)	9.84 (21.7)	1,830 (4.03)	860 (1580)	1280 (2340)	113	3.0	3.2	60	215 (7.6)

[a/] Aldrin content of the ~ 19% granule formulation, based on an average aldrin concentration of 18.7%.

[b/] The flame temperature was observed at a point ~ 15 cm (6 in.) in from the front wall of the incinerator.

[c/] Calculated according to Method 3 of "Standards of Performance for New Stationary Sources," Federal Register, 36(247):24876-24895, 23 December 1971.

[d/] Retention time is defined as $\frac{V}{v}$, where v is the wet off-gas flow rate from the incinerator at the respective chamber temperature and pressure, and V is the volume of that chamber.

[e/] As dry gas at one atmosphere pressure, and 21.1°C (70°F).

Table 38. RESIDUE AND OFF-GAS CHARACTERISTICS--19% ALDRIN GRANULE EXPERIMENTS

Run No.	Pesticide feed rate		Solid residues						Ratio of residues	
			Primary chamber			Second chamber				
	~ 19% Granule formulation kg/hr (lb/hr)	Contained aldrin[a] g/hr	Total kg/hr (lb/hr)	Aldrin conc. ppm	Total species[b] conc. ppm	Total g/hr	Aldrin conc. ppm	Total species[b] conc. ppm	Primary chamber to second chamber	Total residue to total amount fed
A	9.98 (22.0)	1,870	5.53 (12.2)	0.30	0.34	190	7.45	0.45	28.7	0.57
B	9.12 (20.1)	1,700	5.31 (11.7)	0.02	0.06	190	0.45	1.08	28.5	0.60
C	19.55 (43.1)	3,660	12.15 (26.8)	0.08	0.81	280	0.10	0.16	43.2	0.64
D	20.09 (44.3)	3,760	12.29 (27.1)	0.05	0.63	330	0.12	0.13	37.1	0.63
E	19.50 (43.0)	3,650	11.25 (24.8)	N.D.[d]	0.05	390	2.50	2.81	28.9	0.60
F	9.84 (21.7)	1,840	5.99 (13.2)	N.D.	0.20	280	0.55	0.21	21.5	0.64

Run No.	Aldrin content of off-gas g/hr	Aldrin content of solid residues g/hr	Total aldrt. content of off-gas and solid residues g/hr	Total species[b] content of off-gas g/hr	Total species[b] content of solid residues g/hr	Total species[b] content of off-gas and solid residues g/hr	Ratio of aldrin in off-gas to to total aldrin fed	Ratio of total species[b] in off-gas to total aldrin fed	Incineration efficiency[c] %	
									Aldrin	Total species[b]
A	3.9×10^{-4}	2.8×10^{-3}	3.2×10^{-3}	3.3×10^{-3}	3.1×10^{-3}	6×10^{-3}	2.1×10^{-7}	1.8×10^{-6}	> 99.99	> 99.99
B	2.7×10^{-2}	1.5×10^{-4}	2.7×10^{-2}	3.4×10^{-2}	3.0×10^{-4}	3.4×10^{-2}	1.6×10^{-5}	2.0×10^{-5}	> 99.99	> 99.99
C	8×10^{-4}	1.0×10^{-2}	1.0×10^{-2}	5×10^{-3}	1.0×10^{-2}	1.5×10^{-2}	2.3×10^{-7}	1.4×10^{-6}	> 99.99	> 99.99
D	2.7×10^{-4}	7×10^{-4}	9×10^{-4}	3.6×10^{-3}	8×10^{-3}	1.2×10^{-2}	7×10^{-8}	1.0×10^{-6}	> 99.99	> 99.99
E	1.2×10^{-3}	1.0×10^{-3}	2.1×10^{-3}	3.6×10^{-3}	1.6×10^{-3}	5×10^{-3}	3.3×10^{-7}	9×10^{-7}	> 99.99	> 99.99
F	3.5×10^{-5}	1.4×10^{-5}	4.9×10^{-5}	1.5×10^{-3}	1.3×10^{-3}	2.8×10^{-3}	1.9×10^{-8}	8×10^{-7}	> 99.99	> 99.99

---

[a] Actual aldrin content of the ~ 19% granule formulation.

[b] Aldrin plus all other chlorinated hydrocarbon species detected.

[c] Efficiency is defined as $\left[1 - \frac{\text{quantity out}}{\text{quantity in}}\right] \times 100$ where the quantity out is evaluated at Sample Points Nos. ② (the incinerator off-gas) and ③ (solid residues), and the quantity in is evaluated at Sample Point No. ① (the incinerator feed). Efficiencies have been calculated based on (a) aldrin only and (b) the total chlorinated hydrocarbon species detected at Sample Points Nos. ② and ③.

[d] Not detected.

Table 39. OFF-GAS COMPOSITION--19% ALDRIN GRANULE INCINERATION[a]

Run No.	Adrin mg/m^3	Total species[b] mg/m^3	Total hydrocarbons analyzer: Total hydrocarbons ppm	Total hydrocarbons analyzer: CO ppm	Total hydrocarbons analyzer: CH_4 ppm	Orsat analyzer: O_2 vol. %	Orsat analyzer: CO_2 vol. %	Orsat analyzer: CO vol. %	Moisture vol. %
A	2.0×10^{-3}	1.7×10^{-2}	187	2,970	103	7.1	10.2	0.0	3.0
B	1.1×10^{-1}	1.4×10^{-1}	6	269	2	13.0	6.0	0.0	12.5
C	6.5×10^{-3}	2.7×10^{-2}	18	1,490	12	9.7	8.8	0.0	7.2
D	1.0×10^{-3}	1.3×10^{-2}	20	313	3	11.6	7.3	0.0	5.9
E	3.6×10^{-3}	9.5×10^{-3}	4	241	2	11.6	7.2	0.0	8.0
F	1.7×10^{-4}	7.3×10^{-3}	< 1	13	< 1	11.4	7.3	0.0	4.5

---

[a] As dry gas at one atmosphere pressure, and 21.1°C (70°F).

[b] Aldrin plus all other chlorinated hydrocarbon species detected.

Table 40. PARTICULATE SAMPLING SUMMARY--19% ALDRIN GRANULE EXPERIMENTS

Description	A	B	C	D	E	F
Vol. dry gas - std. cond., nm^3	0.421	0.518	0.395	0.391	0.638	0.376
Percent moisture by vol.	3.0	8.5	7.2	5.9	8.0	4.5
Avg. stack temperature, °C	283.5	270.8	206.5	320.6	378.9	242.4
Stk. flow rate, dry, std. cn., nm^3/min	3.5	4.5	3.3	4.6	6.3	3.6
Actual stack flow rate, m^3/min	6.9	9.0	5.7	10.0	15.3	6.6
Percent isokinetic	116.2	111.1	114.6	80.4	97.4	98.5
Percent excess air	48	155	80	119	118	114
Particulates - partial catch						
Particulate wt. - partial, mg	635	310	645	285	629	417
Part. load - ptl., std. cn., mg/nm^3	1,500	598	1,630	727	983	722
Part. load - ptl., stk. cn., mg/m^3	760	297	935	339	404	390
Partic. emis. - partial, kg/hr	0.313	0.160	0.322	0.203	0.370	0.155
Particulates - total catch						
Particulate wt. - total, mg	656	368	712	370	757	487
Part. load - ttl., std. cn., mg/nm^3	1,550	709	1,800	946	1,180	842
Part. load - ttl., std. cn., corrected to 12% CO_2, mg/nm^3	1,830	1,420	2,450	1,560	1,970	1,380
Part. load - ttl., stk. cn., mg/m^3	786	351	1,030	441	486	455
Partic. emis. - total, kg/hr	0.323	0.189	0.356	0.264	0.445	0.181
Percent impinger catch	3.30	15.59	9.41	23.13	16.88	14.27

Table 41. OPERATIONAL DATA SUMMARY--19% ALDRIN GRANULE EXPERIMENTS

Run No.	A	B	C	D	E	F
Temperature °C (°F)						
Primary chamber (Thermocouple No. ①)	1100 (2020)	960 (1730)	850 (1560)	960 (1760)	1050 (1930)	850 (1560)
Primary chamber (Thermocouple No. ②)	1140 (2080)	970 (1780)	850 (1560)	990 (1820)	1100 (2020)	860 (1580)
Primary chamber (Thermocouple No. ③)	1150 (2100)	980 (1800)	890 (1630)	1030 (1890)	1090 (1990)	860 (1580)
Second chamber (Thermocouple No. ④)	960 (1760)	780 (1440)	700 (1300)	830 (1520)	920 (1680)	730 (1350)
Second chamber (Thermocouple No. ⑤)	590 (1100)	410 (770)	390 (730)	520 (960)	630 (1160)	460 (830)
Sample Point No. ② (Thermocouple No. ⑥)	360 (650)	290 (560)	240 (470)	340 (650)	390 (740)	290 (560)
Pressures						
Draft (Manometer No. △1), pascals (in H_2O) gauge	12 (0.050)	29 (0.115)	14 (0.055)	37 (0.150)	51 (0.205)	12 (0.050)
Burner operation pressure, pascals (psi) gauge	7.4×10^5 (108)	7.6×10^5 (110)	8.1×10^5 (117)	8.0×10^5 (116)	8.0×10^5 (116)	8.1×10^5 (117)
Pesticide injection air, pascals (psi) gauge	6×10^4 (9)	6×10^4 (9)	6×10^4 (8)	6×10^4 (9)	7×10^4 (10)	6×10^4 (9)

Stack velocities are normally higher than those existing in the pilot-scale incinerator, especially for those tests conducted at low feed rates. Because the Method 5 train is designed for sampling stacks with typical velocities, it is difficult to maintain isokinetic sampling.

Runs A, B, and C were sampled at rates higher than isokinetic. This would increase the proportion of large particles and increase the grain loading. Run D was lower than isokinetic which would decrease the large particles and lower the apparent grain loading. Runs E and F were in the acceptable range and should be representative of the actual loadings. This is consistent with the grain loading reported in Table 40. The particle loading is reported in mg/m^3 (gr/dscf). The data indicate that the true grain loading on the system is in the 1,300 to 1,900 mg/m^3 (0.6 to 0.8 gr/dscf) range and is not affected by the fuel oil feed rate. Grain loadings in this range are typical of those normally found in a well operated incinerator without control devices.

These results indicate that an incinerator, if required to meet federal regulations while combusting this granular aldrin formulation, would require emission control.

The last item of direct importance to this program is shown in the last line, Percent Impinger Catch. The impinger catch consists of particles which pass through the sample filter (less than 0.8 μ) and organic vapors collected in the impinger solvent. The impinger catch indicates that a much larger fraction of the total discharge from aldrin granular incineration consists of organic volatiles and very fine particulates than from incineration of DDT dust (see Table 41).

Upon completion of the aldrin experiments the interior surfaces of the incinerator and duck work were inspected for any significant deposits. Samples were taken of a thin layer of residue that had deposited on the walls of the stack from the incinerator and in the horizontal run of duct leading to the scrubber system. Neither aldrin nor any of the major components of DDT (p,p'-DDT, o, p'-DDT, p,p'-DDE, o,p'-DDE, p,p'-DDD, and o,p'-DDD) were detected in these samples.

DISCUSSION

No problems were encountered with the incineration of aldrin. It should be noted, however, that the solid residue left in the primary chamber of the incinerator when incinerating the granular formulation at the higher temperatures became very hard and compacted. In fact, it had to be chipped out of the incinerator and ground before being analyzed.

References

1. Zweig, G., (ed.), Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives, Vol. II, Insecticides, Vol. III, Fungicides, Nematocides and Soil Fumigants, Rodenticides and Food and Feed Additives, and Vol. IV, Herbicides, Academic Press, New York (1964).

2. Riemschneider, R., "The Chemistry of the Insecticides of the Diene Group," World Review of Pest Control, 4(29):29-61 (1963).

3. Manufacturing Chemists Association, Laboratory Waste Disposal Manual, 2nd ed. (September 1969).

4. Putnam, R. C., F. Ellison, R. Protzmann, and J. Hilovsky, "Organic Pesticides and Pesticide Containers--A Study of Their Decontamination and Combustion," Foster D. Small, Inc., Final Report on Contract No. CPE 69-140 (1971).

5. von Rümker, R., E. W. Lawless, and A. F. Meiners, "Production, Distribution, Use and Environmental Impact Potential of Selected Pesticides," Final Report, Contract No. EQC-311 for Council on Environmental Quality, Washington, D.C. (1974).

6. Federal Register, 36(247):24876-24895 (23 December 1971).

III. PICLORAM

PESTICIDE DESCRIPTION

Physical Properties

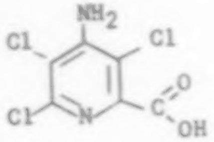
Chemical Name: 4-Amino-3,5,6-trichloropicolinic acid

Common Name: Picloram

Trade Names: Tordon®, 101 Mixture®, Tordon® 10K, Tordon® 22K, Borolin®

Pesticide Class: Systemic herbicide

Structural Formula:



Empirical Formula: $C_6H_3Cl_3N_2O_2$

Molecular Weight: 241.5

Melting Point: Decomposes at 215°C

Boiling Point: Decomposes

Vapor Pressure: at 35°C, 6.16×10^{-7} mm Hg

Solubility: ppm at 25°C, water - 430; isopropyl alcohol - 5,500, acetone - 20,000; xylene - 160; kerosene - 10.

Physical State: Powder

Color: White

Odor: Chlorine like

Stability: Stable

Corrosive Action: Low

Chemical Properties[1]

Incineration at 1000°C for 2 sec is suggested for thermal decomposition. Alternatively, the free acid can be precipitated from its solutions by addition of a mineral acid. The concentrated acid can then be incinerated and the dilute residual solution disposed of in an area where several years' persistence in the soil can be tolerated.

Production and Use

Picloram is effective against a wide variety of herbaceous weeds and woody plants, although most grasses are resistant. Estimated 1972 domestic production was 3 million pounds (Lawless et al.[2]).

Picloram has been available as pellets, as a liquid concentrate, as well as in combination with 2,4-D and 2,4,5-T.

FORMULATIONS TESTED

Picloram was tested using both liquid and solid formulations: a 21.5% picloram liquid and a 10% pellet formulation.

21.5% Liquid Formulation

Name: Tordon® 22K Weed Killer

Manufacturer: The Dow Chemical Company, Midland, Michigan

Composition: Active ingredients (by weight)

Picloram (4-amino-3,5,6-trichloropicolinic acid as the potassium salt	24.9%*
Inert ingredient	75.1%
Total	100.0%

---

* Acid equivalent 21.5% (2 lb/gal).

Registration: EPA Reg. No. 464-323-AA

Lot No.: MM 810764

10% Pellet formulation

Name: Tordon 10K Pellets

Manufacturer: The Dow Chemical Company, Midland, Michigan

Composition: Active ingredient (by weight)

Picloram (4-amino-3,5,6-trichloropicolinic acid as the potassium salt)	11.6%*
Inert ingredients	88.4%
Total	100.0%

---

* Acid equivalent 10%.

Registration: EPA Reg. No. 464-320-AA

Lot No.: F-12083B, F-12303A, F-10223C

Particle Size Specifications: Extruded on bentonite clay, 4 mm (5/32 in.) in diameter x 8 mm (5/16 in.) long

PRELIMINARY THERMAL ANALYSIS

The laboratory thermal analyses of picloram gave the following results:

Sample	Test	Test method	Result
Picloram (technical grade)	Calorific value	ASTM D-2015	1.392×10^7 J/kg (5,990 Btu/lb)
	Sulfur	ASTM D-129	0.82%
Picloram Pellet (10% acid equivalent)	Calorific value	ASTM D-2015	1.120×10^6 J/kg (482 Btu/lb) (no sulfur correction)
Picloram Solution (21.5% acid equivalent)	Calorific value	ASTM D-2015	7.813×10^6 J/kg (3,362 Btu/lb)
	Sulfur	ASTM D-129	0.16%

Differential thermal analysis (DTA) of the picloram pellets showed one endotherm at about 90°C (see Figure 26). Beyond 90°C, the sample showed a continuous decomposition process all the way to the instrument operational limit (400°C). This decomposition process was supported by the weight loss shown by thermal gravimetric analysis (TGA). The total weight loss up to 400°C was approximately 12%, which corresponds to the ~ 11.6% picloram salt content of the pellets (see Figure 27).

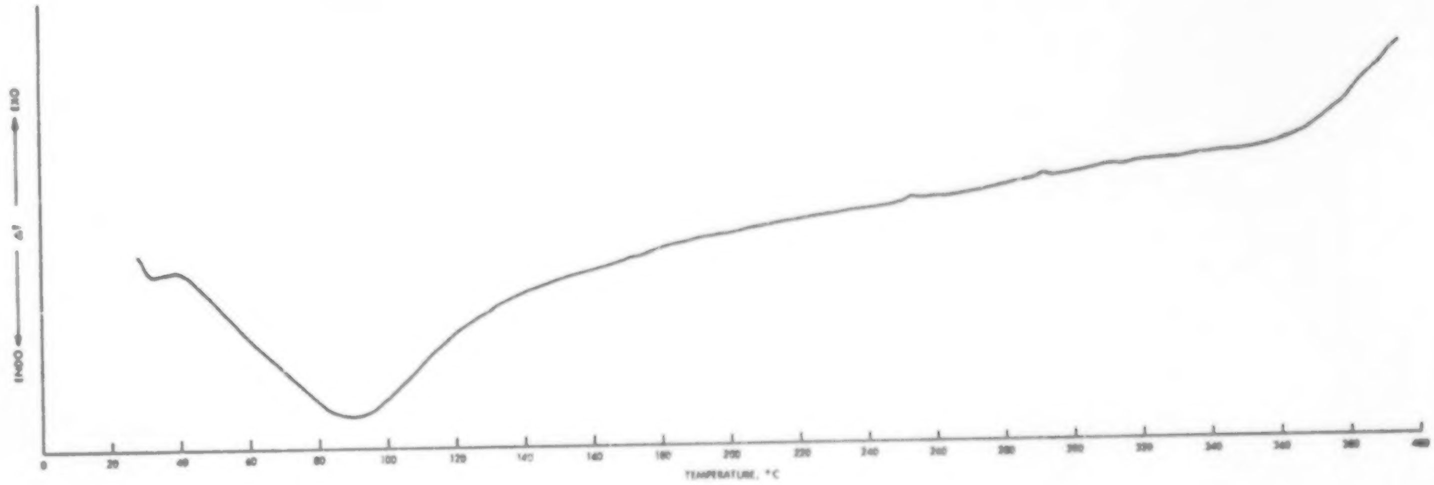
DTA of a sample of recrystallized picloram obtained by the evaporation of the 21.5% potassium salt formulation showed endotherms at 68 to 80°C, and 144 to 154°C (see Figure 28). Once past the second endotherm, decomposition started and exotherms at 222, 302, and 353°C were observed. The decomposition process continued to the instrument operational limit (400°C). A check on the TGA data showed no significant weight loss at the two endotherm temperature ranges, thus, indicating possible phase changes. However, from 180 to 360°C, about 60% weight loss was observed. Weight loss continued from 360 to 500°C and about 800 to 900°C. At 900°C virtually no sample remained. Therefore, it is very probable that picloram would be destroyed before 900°C (see Figure 29).

Kennedy et al.[3] also conducted DTA of picloram. The results of their analyses were as follows:

	Endotherms	Exotherms
Reference standard	225, 270 and 482°C	None reported
11.6% Picloram solution	145, 160, 171, 173 334, and 355°C	190, 386, 475 and 580°C

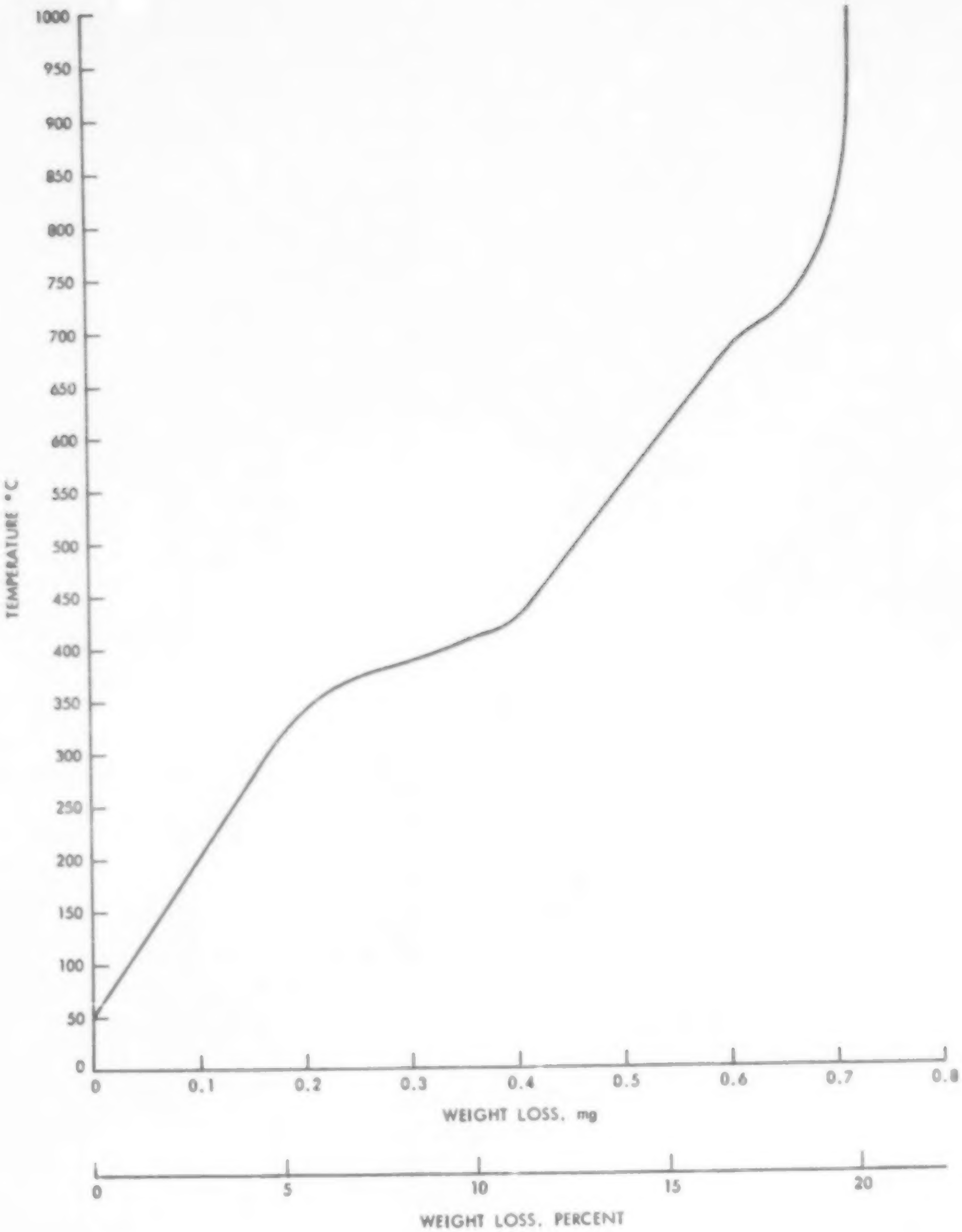
Sensitivity = 25%.

Based on these and other laboratory analyses, Kennedy et al. concluded that the temperatures for complete combustion of the picloram reference standard and solution were 550°C (1022°F) and 640°C (1184°F), respectively.



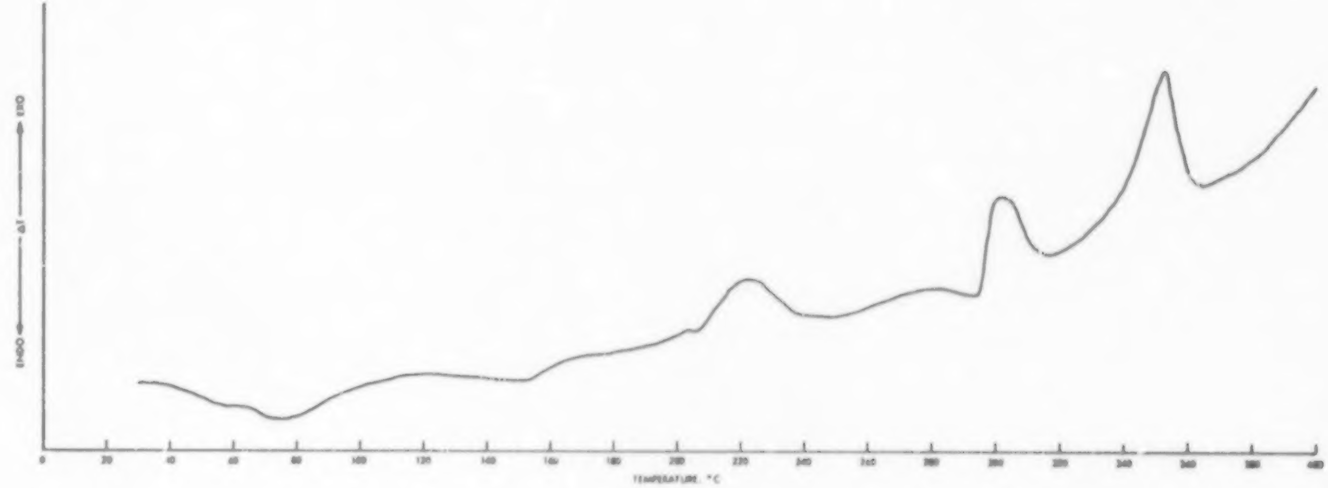
Reference: Empty pan
Prog. mode: Heat
Rate: 10°C/min
Start: 28°C

Figure 26. DTA of picloram pellets.



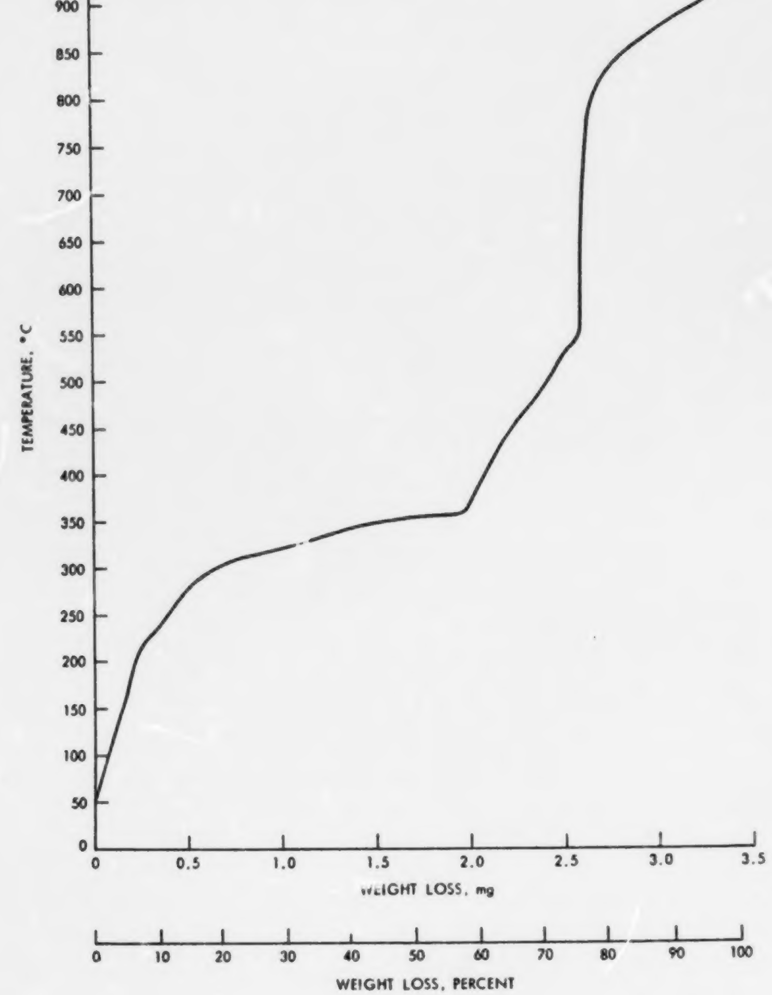
Sample weight: 3.610 mg
Heating rate: 20°C/min
Environment: ~20 ml/min air (20% O_2, 80% N_2)

Figure 27. TGA of picloram pellets.



Reference: Empty pan
Prog. mode: Heat
Rate: 10°C/min
Start: 30°C

Figure 28. DTA of recrystallized picloram.



Sample weight: 3.354 mg
Heating rate: 20°C/min
Environment: ~ 20 ml/min air (20% O_2, 80% N_2)

Figure 29. TGA of recrystallized picloram.

METHODS OF ANALYSIS

Apparatus

A Micro-Tek 2000R gas chromatograph equipped with a 3-ft, 4 mm I.D. glass column (packed with 1.5% OV-17 + 1.95% QF-1 on 80/100 mesh Supelcoport from Supelco, Inc., Bellefonte, Pennsylvania), and a tritium electron capture detector, maintained at a voltage of 15 V DC, were used for gas chromatographic analysis. Chromatographic operating conditions were: injector temperature, 225°C; column temperature, 190°C; detector temperature, 180°C; carrier flow rate, 100 ml/min, N_2; and purge flow rate, 200 ml/min, N_2.

A Varian G-2000 strip chart recorder was used to record the chromatograms.

Reagents and Materials

The picloram standard used was obtained from the Pesticides and Toxic Substances Effects Laboratory, USEPA, Research Triangle Park, North Carolina. The solid standard, 4-amino-3,5,6-trichloro-2-picolinic acid, methyl ester (picloram methyl ester), used for preparing standards for gas chromatographic analysis was obtained from Dow Chemical Company, Midland, Michigan. N-methyl-N-nitroso-N'-nitroquanidine used for preparing diazomethane for methylation of samples was procured from Pfaltz and Bauer, Flushing, New York. Solvents used were pesticide grade diethyl ether (Fisher Scientific) in preparing diazomethane, pesticide grade 2,2,4-trimethylpentane (Mallinckrodt) for standard solutions, pesticide grade hexane (Matheson, Coleman, Bell) for extraction of hexylene glycol traps from the second stage scrubber, and pesticide grade benzene (Fisher Scientific) for all samples after methylation.

Diazomethane, used for methylation of picloram, was prepared in the following manner: 2.3 g of analytical reagent grade potassium hydroxide (Fisher Scientific) was dissolved in 2.3 g deionized distilled water and added to 25 ml of ether, 1.5 g of N-methyl-N-nitroso-N'-nitroguanidine (ether washed) was added very slowly to the KOH-ether in an Erlenmeyer flask. The guanidine went through the ether layer and dissolved in the KOH layer, releasing diazomethane into the ether. The ether layer was carefully decanted and saved and the KOH layer properly disposed. (Note: Diazomethane and N-methyl-N-nitroso-N'-nitroguanidine are carcinogenic and explosive; due care was and must be exercised.)

Standards and Calibration Curve

The solid standards, picloram methyl ester, obtained from Dow Chemical Company, was used to prepare stock standard of 100 μg/ml and appropriate dilutions were made to produce a linear curve (linear range used: 0 to 100 pg).

Procedure for Sample Preparation

All samples from liquid formulation tests, excluding the hexylene glycol samples from the second stage scrubber, were taken just to dryness. One milliliter of diazomethane was added to each dried sample and allowed to sit uncovered (in a hood) for at least 2 hr, so the ether could evaporate, and then capped. Ten milliliters of the hexylene glycol samples were extracted with hexane, the extract was dried, and methylated as above.

The mass of collected particulate was determined for all samples collected from incineration of picloram pellets as follows. Samples were taken to dryness in clean, dessicated, tared 250-ml beakers and dessicated 2 days before final weighing. The residue was extracted and the extract was taken just to dryness and methylated. Twenty milliliters of each of the blank solutions were pipetted into a vial, taken to dryness and methylated. The silica gel impinger was extracted with reagent grade 2-propanol (Fisher Scientific); 10 ml of this extract was taken to dryness and methylated.

All samples were taken up in 5 ml of benzene just prior to gas chromatographic analysis.

Portions of all the residue samples (primary chamber, secondary chamber, etc.) were weighed out, extracted, and the extracts were methylated and analyzed for picloram methyl ester.

Analysis and Discussion

All samples were analyzed for the picloram methyl ester. Unidentified chromatographic peaks were quantitated against the picloram methyl ester calibration curve. (Representative chromatograms are shown in Figure 30).

The sensitivity of the instrument for picloram methyl ester is 10 pg. Based on this sensitivity value and with a 5 μl sample injection for each analysis, the minimum detectable value for a 20-ml sample solution is 40 ng. However, during the analysis samples were very often concentrated to 1 ml, which resulted in a minimum detectable quantity of 2 ng.

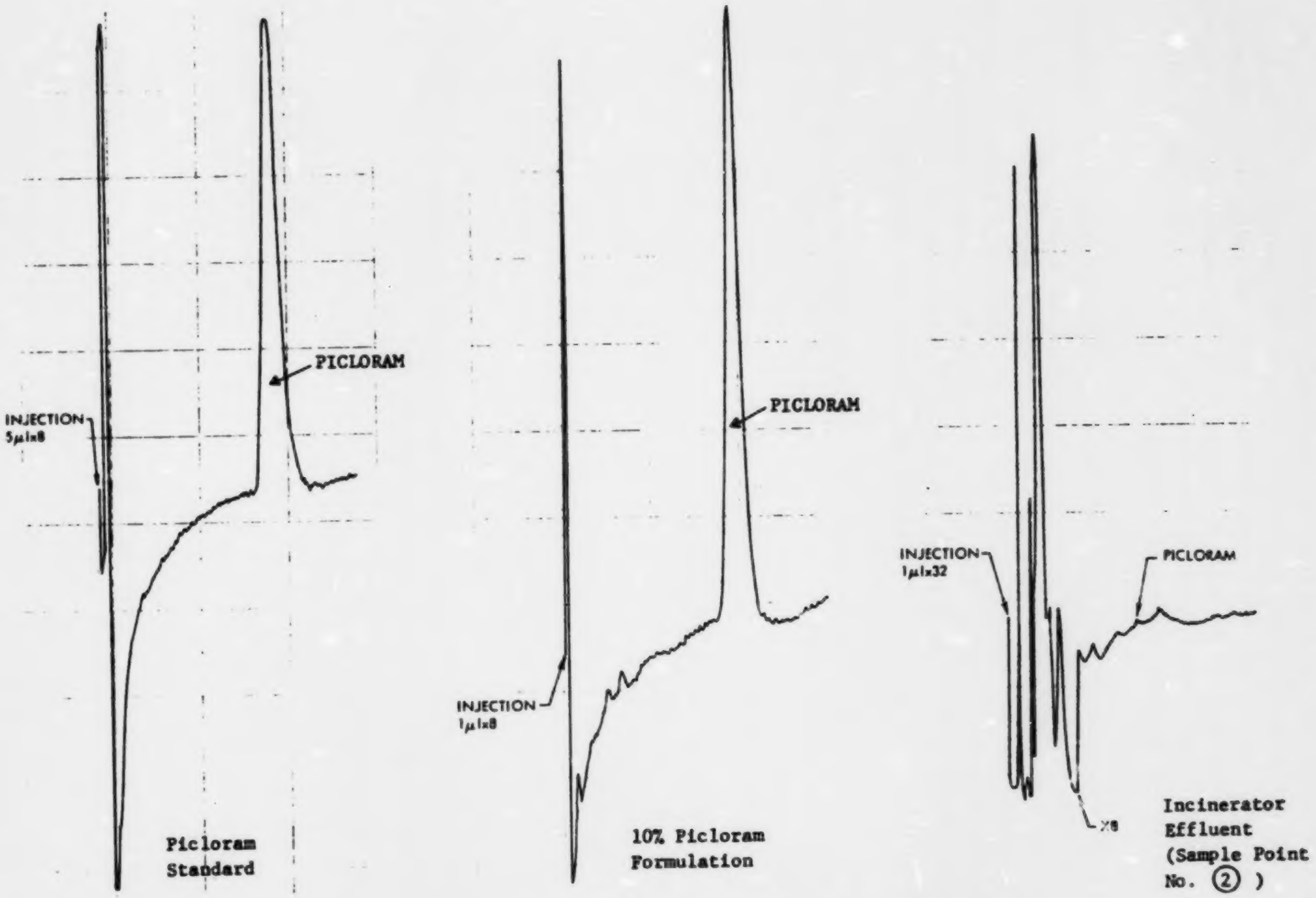


Figure 30. Representative picloram chromatograms.

Prior to adopting the diazomethane esterification of picloram and followed by GC analysis, two other methods of analysis were also examined. The first method was to analyze the silylation product of picloram by gas chromatography. Silylation reagent Trizil "Z" (N-tri-methylsilylimidazole) was used, and reaction products were analyzed with electron capture GC. This method of analysis was given up because of interferences due to a large number of peaks from the samples and the reagent, and also because of lengthy retention times.

The second method examined was analysis of picloram by a luminescence technique. An Aminco Bowman spectrophotofluorometer was used to measure the excitation and emission spectra. Unfortunately, picloram does not show any natural fluorescence at 298 and 77°K; however, strong phosphorescence was observed at 77°K. The phosphorescence method was not employed because quantitative phosphorescence data are difficult to obtain unless specially designed sample cells are used.[4,5]

Before using the diazomethane technique of forming methyl picloram ester, esterification with boron trichloride 2-chloroethanol reagent at elevated temperature was examined. The esterification yield by this approach was so low that this method was not employed.

In order to check if there were organic acids or alcohols, besides residual picloram formed after incineration, chromatograms were collected for selected samples before and after the esterification. No differences, except the picloram ester peak, were observed in these chromatograms which indicates that the volatile unidentified species were probably chlorinated hydrocarbons formed from incineration of picloram.

Esterification of picloram with diazomethane employed in this study generally gave a yield of over 90%.

TEST CONDITIONS AND RESULTS

Initially, seven experiments were made using a water-based liquid formulation of picloram (24.9% 4-amino-3,5,6-trichloropicolinic acid as the potassium salt, 21.5% acid equivalent). Because this formulation was not miscible with No. 2 fuel oil, a modification of the incinerator feed system was required (all miscible pesticide formulations were mixed in the appropriate ratio with fuel oil and injected through the primary burner position of the incinerator with an oil burner). Two separate systems were used to inject fuel oil and the picloram formulation into the primary chamber of the incinerator on a horizontal plane. A standard oil burner was used for the fuel oil.

The undiluted picloram was pumped into the incinerator through a fuel oil nozzle of the same type being used in the oil burner. These injection systems were positioned so that the picloram and the flame from the fuel oil burner impinged at an angle of 30 degrees and at a point about 8 cm (3 in.) from the front wall of the incinerator. This is the same configuration that is used to inject solid pesticide formulations.

The results of the seven initial tests (as well as two subsequent tests) have been summarized in Tables 42 through 45.

Two efficiencies of combustion were calculated to evaluate the results of these tests. The first considered only the picloram in the incinerator input and discharge. This efficiency calculation showed that > 99.99% of the picloram injected into the incinerator was at least partially degraded at all temperatures tested, 530 to 1030°C (990 to 1880°F); see Table 43. This is not unexpected, as picloram has been reported to decompose at about 216°C (420°F).[6]

The second efficiency calculation includes not only the picloram that is left in the incinerator effluent but also the other chemical species trapped in the sample collection system. Using this calculation, only the two tests (of the seven initial tests) conducted at 1010 and 1030°C (1850 and 1880°F) showed an efficiency of > 99.99%. As will be discussed later, these two tests also showed significantly lower concentrations (and quantities) of cyanide in the incinerator effluent.

Small quantities of residue were found in the primary and secondary chambers of the incinerator after each of the four tests conducted at lower temperatures, 530 to 800°C (990 to 1470°C). Analyses of these residues gave the following results:

	Primary chamber residue			Second chamber residue		
Run No.	Total g/hr	Picloram ppm	Total species[a] ppm	Total g/hr	Picloram ppm	Total species ppm
1	21	ND[b]	0.2	-	-	-
2	397	1.7	3.0	43	0.1	6.9
3	298	ND	0.8	29	ND	4.2
4	-	-	-	-	-	-
5	-	-	-	-	-	-
6	-	-	-	-	-	-
7	628	1.1	7.1	460	< 0.1	< 4.5

---

[a] Picloram plus all other chlorinated hydrocarbon species detected.

[b] Not detected.

Table 42. SUMMARY OF 21.5% PICLORAM LIQUID EXPERIMENTS

Run No.	Fuel oil rate		Picloram rate			Primary chamber temperature °C (°F)	Flame temperature[b] °C (°F)	Excess air[c] %	Retention time[d] sec		Sampling time min	Off-gas flow rate[e] m^3/hr (1,000's of SCFM)
	Nominal burner size ℓ/hr (gal/hr)	Actual feed rate ℓ/hr (gal/hr)	Nominal nozzle size ℓ/hr (gal/hr)	Actual feed rate ℓ/hr (gal/hr)	Picloram rate[a] g/hr (lb/hr)				Primary chamber	Second chamber		
1	2.8 (0.75)	2.57 (0.68)	11.4 (3.0)	8.78 (2.32)	1,870 (4.12)	530 (990)	NA[f]	298	7.6	8.0	30	116 (4.1)
2	3.8 (1.0)	3.60 (0.95)	9.5 (2.5)	6.43 (1.70)	1.380 (3.05)	600 (1120)	NA	193	6.7	6.9	30	110 (3.9)
3	5.7 (1.5)	5.72 (1.51)	18.9 (5.0)	7.31 (1.93)	1,510 (3.33)	630 (1160)	NA	187	6.6	6.8	30	113 (4.0)
4	11.4 (3.0)	9.08 (2.40)	9.5 (2.5)	5.72 (1.51)	1,290 (2.84)	930 (1700)	NA	62	3.9	4.0	30	150 (5.3)
5	13.2 (3.5)	12.49 (3.30)	9.5 (2.5)	5.56 (1.47)	1,110 (2.45)	1010 (1850)	NA	130	1.4	1.4	30	391 (13.8)
6	13.2 (3.5)	12.30 (3.25)	20.8 (5.5)	13.59 (3.59)	3,470 (7.64)	1030 (1880)	NA	116	1.2	1.2	28.5	433 (15.3)
7	11.4 (3.0)	8.36 (2.21)	20.8 (5.5)	13.51 (3.57)	2,230 (4.92)	800 (1470)	NA	77	6.0	5.8	30	108 (3.8)
8	9.5 (2.5)	9.08 (2.40)	20.8 (5.5)	13.10 (3.46)	3,270 (7.22)	1000 (1840)	1090 (2000)	114	1.9	1.8	28.5	303 (10.7)
9	9.5 (2.5)	9.16 (2.42)	20.8 (5.5)	13.25 (3.50)	2,450 (5.40)	1010 (1850)	1150 (2110)	50	2.6	2.5	30	204 (7.2)

---

[a] Actual picloram content of the incinerator feed.

[b] The flame temperature was observed at a point approximately 15 cm (6 in.) in from the front wall of the incinerator (see Figure B-1).

[c] Calculated according to Method 3 of "Standards of Performance for New Stationary Sources," Federal Register, 36(247):24876-24895, 23 December 1971.

[d] Retention time is defined as $\frac{V}{v}$, where v is the wet off-gas flow rate from the incinerator at the respective chamber temperature and pressure, and V is the volume of that chamber.

[e] As dry gas at one atmosphere pressure, and 21.1°C (70°F).

[f] Not determined.

Table 43. INCINERATION EFFICIENCY--21.5% PICLORAM LIQUID FORMULATION

Run No.	Picloram feed rate[a] g/hr	Picloram content of off-gas g/hr	Ratio of picloram in off-gas to picloram fed	Total speices[b] content of off-gas g/hr	Ratio of total species[c] in off-gas to total picloram fed	Incineration efficiency[c] %	
						Picloram	Total species[b]
1	1,870	3×10^{-3}	2×10^{-6}	3	2×10^{-3}	> 99.99	> 99.83
2	1,380	2×10^{-3}	1×10^{-6}	0.6	4×10^{-4}	> 99.99	> 99.95
3	1,510	5×10^{-4}	3×10^{-7}	6	4×10^{-3}	> 99.99	> 99.63
4	1,290	2×10^{-3}	2×10^{-6}	0.3	2×10^{-4}	> 99.99	> 99.98
5	1,110	2.6×10^{-2}	2.3×10^{-5}	0.040	3.6×10^{-5}	> 99.99	> 99.99
6	3,470	7×10^{-3}	2.0×10^{-6}	0.044	1.3×10^{-5}	> 99.99	> 99.99
7	2,230	1×10^{-3}	4×10^{-7}	5	2×10^{-3}	> 99.99	> 99.78
8	3,270	3.0×10^{-2}	9×10^{-6}	0.035	1.1×10^{-5}	> 99.99	> 99.99
9	2,450	9×10^{-2}	3.7×10^{-5}	0.10	4.1×10^{-5}	> 99.99	> 99.99

---

a/ Actual picloram content of the incinerator feed.
b/ Picloram plus all other chlorinated organic species detected.

c/ Efficiency is defined as $\left[1 - \frac{\text{quantity \underline{out}}}{\text{quantity \underline{in}}}\right] \times 100$, where the quantity out is evaluated as Sample Point No. ② (the effluent gas), and the quantity in is evaluated at Sample Point No. ① (the incinerator feed). Efficiencies have been calculated based on (a) picloram only, and (b) the total chlorinated organic species detected at Sample Point No. ② .

Table 44. OFF-GAS COMPOSITION--21.5% PICLORAM LIQUID INCINERATION[a]

						Total hydrocarbons analyzer			Orsat analyzer			
Run No.	Pichloram mg/m^3	Total species[c] mg/m^3	CN$^-$ mg/m^3	SO$_2$ mg/m^3	NO$_x$[e] mg/m^3	Total hydrocarbons ppm	CO ppm	CH$_4$ ppm	O$_2$ vol. %	CO$_2$ vol. %	CO vol. %	Moisture vol. %
1	2.7×10^{-2}	26	689	20	110	708	3,230	> 842[g]	16.1	2.8	0.0	4.6
2	1.5×10^{-2}	5.6	906	ND[d]	48	732	> 4,630[g]	> 875[g]	14.3	3.6	0.0	8.3
3	$< 4.3 \times 10^{-3}$[b]	49	211	5	95	712	3,510	> 851[g]	14.2	3.3	0.0	7.1
4	1.7×10^{-2}	1.7	98	9	ND	625	3,660	> 943[g]	8.4	8.1	0.0	3.2
5	6.6×10^{-2}	0.10	< 1	ND	310	686	1,490	244	12.2	6.5	0.0	4.6
6	1.6×10^{-2}	0.10	< 1	9	1,860	37	< 1	4	11.7	5.7	0.0	5.8
7	$< 9 \times 10^{-3}$[b]	44	967	3	553	704	3,680	> 962[g]	10.5	6.1	2.6	5.1
8	1.0×10^{-1}	0.12	< 1	162	NA[f]	13	< 1	< 1	11.4	7.2	0.0	5.8
9	4.4×10^{-1}	0.49	2	253	36	8	18	< 1	7.2	10.4	0.0	11.2

---

[a] As dry gas at one atmosphere pressure and 21.1°C (70°F).

[b] Picloram was not detected. The value given represents the detection limit for picloram in the respective sample.

[c] Picloram plus all other chlorinated organic species detected.

[d] Not detected.

[e] Calculated as NO$_2$.

[f] No analysis.

[g] Upper detection limit.

Table 45. OPERATIONAL DATA SUMMARY--21.5% PICLORAM LIQUID EXPERIMENTS

Run No.	1	2	3	4	5
Temperature °C (°F)					
Primary chamber (Thermocouple No. ①)	530 (990)	590 (1100)	610 (1130)	890 (1640)	900 (1660)
Primary chamber (Thermocouple No. ②)	400 (760)	590 (1090)	600 (1110)	920 (1630)	940 (1730)
Primary chamber (Thermocouple No. ③)	490 (920)	600 (1120)	630 (1160)	930 (1700)	1010 (1850)
Second chamber (Thermocouple No. ④)	400 (760)	530 (990)	550 (1030)	800 (1480)	840 (1540)
Second chamber (Thermocouple No. ⑤)	220 (430)	280 (540)	290 (560)	490 (910)	600 (1120)
Sample Point No. ② (Thermocouple No. ⑥)	150 (300)	170 (340)	180 (350)	290 (560)	420 (790)
Pressures					
Draft (Manometer No. △1), pascals (in. H_2O) gauge	12 (0.050)	11 (0.045)	12 (0.050)	12 (0.050)	46 (0.185)
Fuel oil burner pressure, pascals (psi) gauge	NA[a]	NA	NA	NA	8.0×10^5 (116)
Pesticide injection air pressure, pascals (psi) gauge	4.0×10^5 (58)	4.1×10^5 (60)	4.4×10^5 (64)	4.5×10^5 (65)	4.4×10^5 (64)
Scrubber liquids[b]					
1st Stage, H_2O scrubber					
Volume, ℓ (gal.)	1120 (297)	1290 (340)	1230 (325)	1240 (327)	1180 (313)
Picloram conc., mg/ℓ	$< 2 \times 10^{-3}$[e]	$< 2 \times 10^{-3}$[e]	$< 2 \times 10^{-3}$[e]	2×10^{-3}	1×10^{-2}
Total species conc.,[c] mg/ℓ	2	2	6	4	2
2nd Stage, hexalene glycol scrubber					
Volume, ℓ (gal.)	84 (22.1)	83 (21.9)	84 (22.1)	84 (22.1)	83 (21.8)
Picloram conc. change, mg/ℓ	$< 2 \times 10^{-3}$[e]	$< 2 \times 10^{-3}$[e]	$< 2 \times 10^{-3}$[e]	$< 3 \times 10^{-3}$[e]	$< 3 \times 10^{-3}$[e]
Total species conc. change,[c] mg/ℓ	9×10^{-1}	2	2	ND[f]	ND
3rd Stage, H_2O scrubber					
Volume, ℓ (gal.)	1990 (526)	2030 (537)	1840 (486)	1880 (497)	1990 (526)
Picloram conc., mg/ℓ	$< 2 \times 10^{-3}$[e]	$< 2 \times 10^{-3}$[e]	$< 2 \times 10^{-3}$[e]	2×10^{-3}	$< 2 \times 10^{-3}$[e]
Total species conc.,[c] mg/ℓ	3×10^{-1}	7×10^{-1}	5×10^{-1}	2×10^{-1}	4×10^{-1}
Scrubber system					
Effluent gas (Sample Point No. ⑨)[d]					
Picloram conc., mg/m^3	$< 2 \times 10^{-2}$[e]	$< 6 \times 10^{-3}$[e]	$< 7 \times 10^{-3}$[e]	$< 7 \times 10^{-3}$[e]	$< 6 \times 10^{-3}$[g]
Total species conc.,[c] mg/m^3	$< 8 \times 10^{-1}$	$< 8 \times 10^{-2}$	$< 2 \times 10^{-1}$	$< 5 \times 10^{-2}$	$< 7 \times 10^{-2}$

Table 45. (Concluded)

Run No.	6	7	8	9
Temperature °C (°F)				
Primary chamber (Thermocouple No. ①)	950 (1740)	770 (1410)	920 (1680)	950 (1740)
Primary chamber (Thermocouple No. ②)	940 (1730)	780 (1430)	910 (1670)	890 (1640)
Primary chamber (Thermocouple No. ③)	1030 (1880)	800 (1470)	1000 (1840)	1010 (1850)
Second chamber (Thermocouple No. ④)	920 (1690)	750 (1390)	900 (1660)	890 (1630)
Second chamber (Thermocouple No. ⑤)	680 (1260)	470 (870)	640 (1180)	650 (1200)
Sample Point No. ② (Thermocouple No. ⑥)	500 (930)	250 (480)	420 (780)	380 (710)
Pressures				
Draft (Manometer No. ⚠1), pascals (in H_2O) gauge	50 (0.200)	12 (0.050)	63 (0.255)	39 (0.155)
Fuel oil burner pressure, pascals (psi) gauge	9.1×10^5 (132)	9.1×10^5 (132)	7.9×10^5 (115)	7.4×10^5 (108)
Pesticide injection air pressure, pascals (psi) gauge	NA	4.6×10^5 (66)	4.1×10^5 (60)	3.7×10^5 (54)
Scrubber liquids[b/]				
1st Stage, H_2O scrubber				
Volume, ℓ (gal.)	1230 (325)	1120 (295)	1140 (302)	1060 (280)
Picloram conc., mg/ℓ	$< 2 \times 10^{-3}$[e/]	2×10^{-2}	NA	NA
Total species conc.,[c/] mg/ℓ	5×10^{-1}	7×10^{-1}	NA	NA
2nd Stage, hexalene glycol scrubber				
Volume, ℓ (gal.)	90 (23.9)	86 (22.8)	99 (26.1)	99 (26.1)
Picloram conc. change, mg/ℓ	2×10^{-3}	2×10^{-3}	NA	NA
Total species conc. change,[c/] mg/ℓ	ND	6×10^{-1}	NA	NA
3rd Stage, H_2O scrubber				
Volume, ℓ (gal.)	1820 (480)	1730 (457)	1780 (469)	1730 (457)
Picloram conc., mg/ℓ	$< 2 \times 10^{-3}$[e/]	3×10^{-3}	NA	NA
Total species conc.,[c/] mg/ℓ	6×10^{-2}	7×10^{-1}	NA	NA
Scrubber system				
Effluent gas (Sample Point No. ⑨)[d/]				
Picloram conc., mg/m^3	$< 8 \times 10^{-3}$[g/]	$< 3 \times 10^{-2}$[g/]	NA	NA
Total species conc.,[c/]	$< 3 \times 10^{-2}$	$< 4 \times 10^{-1}$	NA	NA

[a/] Not determined.

[b/] Scrubber water (Scrubbers 1 and 3) was used once through, while the hexylene glycol (Scrubber 2) was recycled. The concentrations reported for hexylene glycol, therefore, are the concentration changes (increases) detected during the respective tests.

[c/] Picloram plus all other chlorinated organic species detected.

[d/] As the wet gas at one atmosphere pressure and 20°C.

[e/] Picloram not detected. The values given represent the detection limit for picloram in the respective sample.

[f/] No increase detected.

[g/] Picloram not detected in all components (i.e. impingers) of gas sampling train. The value given includes the detectable limit for picloram in these components.

The inclusion (or exclusion) of these residues has no effect on the efficiency of combustion as shown in Table 43.

In order to evaluate the effect of physical form on the efficiency with which picloram can be incinerated, five tests were made using a pellet formulation (~ 11.6% picloram as the potassium salt, 10% as the acid equivalent). Results from these five experiments (as well as subsequent additional tests) are summarized in Tables 46 through 50.

The last of the five initial tests conducted (Run No. E) was made with ground picloram pellets. Approximate size distribution of the ground material was:

Particle size (μ)	Distribution (%)
> 1,680	1.1
1,680 to 1,410	0.8
1,410 to 1,190	6.7
1,190 to 53	78.4
53 to 44	1.0
< 44	12.0

Pictures of the original picloram pellets, as well as residues recovered from the primary chamber of the incinerator after Run No. B, are shown in Figure 31. Residue A is representative of the majority of material found in the primary chamber. Residue B is representative of the top layer of residue found in the primary chamber after the two high-temperature runs (Nos. A and B). Picloram content of Residues A and B from Run No. B was 0.2 and < 0.1 ppm, respectively.

As was done for the experiments using the liquid formulation, two efficiencies of combustion were calculated. The first considers only the quantity of picloram in the incinerator input and discharge. This efficiency calculation showed that > 99.99% of the picloram injected into the incinerator was at least partially degraded at all temperatures tested during the first five tests, 930 to 1020°C (1710 to 1870°F).

Table 46. SUMMARY OF 10% PICLORAM PELLET EXPERIMENTS

	No. 2 fuel oil rate		Pesticide feed rate					Retention time[d] sec			
Run No.	Nominal burner size ℓ/hr (gal/hr)	Actual rate ℓ/hr (gal/hr)	~ 10% Pellet formulation kg/hr (lb/hr)	Contained picloram[a] g/hr (lb/hr)	Primary chamber temperature °C (°F)	Flame temperature[b] °C (°F)	Excess air[c] %	Primary chamber	Second chamber	Sampling time min	Off-gas flow rate[e] m^3/hr (1,000's of SCFH)
A	11.4 (3.0)	9.01 (2.38)	17.42 (38.4)	1,270 (2.8)	1020 (1870)	1140 (2080)	93	1.3	1.4	60	408 (14.4)
B	11.4 (3.0)	9.46 (2.50)	17.24 (38.0)	1,270 (2.8)	930 (1710)	1270 (2320)	170	2.1	2.2	60	300 (10.6)
C	3.8 (1.0)	3.60 (0.95)	16.51 (36.4)	1,180 (2.6)	640 (1190)	1020 (1860)	226	6.9	7.4	60	119 (4.2)
D	3.8 (1.0)	3.44 (0.91)	32.75 (72.2)	2,360 (5.2)	710 (1310)	980 (1800)	227	6.7	7.3	60	113 (4.0)
E	11.4 (3.0)	9.08 (2.40)	32.21 (71.0)	2,360 (5.2)	930 (1700)	870 (1590)	72	4.6	4.9	60	125 (4.4)
F	9.5 (2.5)	9.35 (2.47)	31.84 (70.2)	2,350 (5.2)[f]	950 (1750)	1180 (2160)	75	2.6	2.6	60	232 (8.2)
G	9.5 (2.5)	9.58 (2.53)	30.66 (67.6)	2,270 (5.0)[f]	920 (1680)	1150 (2110)	145	1.9	1.7	60	336 (11.8)

---

[a] Actual content of picloram in the ~ 10% (acid equivalent) pellet formulation.

[b] The flame temperature was observed at a point approximately 15 cm (6 in.) in from the front wall of the incinerator (see Figure B-1).

[c] Calculated according to Method 3 of "Standards of Performance for New Stationary Sources," Federal Register, 36(247):24876-24895, 23 December 1971.

[d] Retention time is defined as $\frac{V}{v}$, where v is the wet off-gas flow rate from the incinerator at the respective chamber temperature and pressure, and V is the volume of that chamber.

[e] As dry gas at one atmosphere pressure, and 21.1°C (70°F).

[f] These values for contained picloram are based on the average content (as determined from Runs Nos. A through E) of 7.4%. Triplicate analysis of the feed material for the two additional tests (Runs Nos. F and G, which were from a different production batch than the initial five tests), showed a picloram content of 0.4%. Other picloram analyses for Runs. Nos. F and G, however, as shown in Table B-III-6, are comparable to earlier test results. Thus, the value of 7.4% has also been used to calculate the picloram content of the feed for Tests F and G.

Table 47. RESIDUE AND OFF-GAS CHARACTERISTICS--10% PICLORAM PELLET EXPERIMENTS

Run No.	Pesticide feed rate		Solid residue						Ratio of total incinerator residue to total charge
			Primary chamber			Second chamber			
	~10% Picloram formulation kg/hr (lb/hr)	Contained picloram[a] g/hr	Total kg/hr (lb/hr)	Picloram conc. ppm	Total species[b] conc. ppm	Total g/hr	Picloram conc. ppm	Total species[b] conc. ppm	
A	17.42 (38.4)	1,270	13.15 (29.0)	1.1	7.1	38	0.08	4.4	0.76
B	17.24 (38.0)	1,270	12.61 (27.8)	0.07	3.0	43	1.4	5.3	0.72
C	16.51 (36.4)	1,180	13.70 (30.2)	0.08	9.0	57	0.3	84.9	0.83
D	32.75 (72.2)	2,360	26.48 (58.4)	0.5	41.1	54	1.1	89.7	0.81
E	32.21 (71.0)	2,360	25.08 (55.3)	0.06	0.3	858	0.6	4.6	0.81
F	31.84 (70.2)	2,360[d]	23.63 (52.1)	0.01	2.5	98	NA[e]	NA	0.74
G	30.66 (67.6)	2,270[d]	23.13 (51.0)	0.4	1.9	73	NA	NA	0.76

Run No.	Picloram content of off-gas g/hr	Picloram content of solid residues g/hr	Total picloram content of off-gas and solid residues g/hr	Total species[b] content of off-gas g/hr	Total species[b] content of solid residues g/hr	Total species[b] content of off-gas and solid residues g/hr	Ratio of picloram in off-gas to total picloram fed	Ratio of total species[b] in off-gas to total picloram fed	Incineration efficiency[c] %	
									Picloram	Total species[b]
A	$< 1 \times 10^{-5}$[f]	1.4×10^{-2}	1.4×10^{-2}	$< 3.2 \times 10^{-3}$	1.1×10^{-1}	1.1×10^{-1}	$< 8 \times 10^{-9}$	2.5×10^{-6}	> 99.99	> 99.99
B	$< 7 \times 10^{-5}$[f]	9×10^{-4}	$< 1.0 \times 10^{-3}$	2.9×10^{-2}	3.9×10^{-2}	7×10^{-2}	$< 5 \times 10^{-8}$	2.3×10^{-5}	> 99.99	> 99.99
C	$< 6 \times 10^{-5}$[f]	1×10^{-3}	$< 1 \times 10^{-3}$	2×10^{-1}	1×10^{-1}	4×10^{-1}	$< 6 \times 10^{-8}$	2×10^{-4}	> 99.99	> 99.96
D	$< 4 \times 10^{-5}$[f]	1×10^{-2}	1×10^{-2}	4×10^{-1}	1	2	2×10^{-8}	2×10^{-4}	> 99.99	> 99.93
E	8×10^{-3}	2×10^{-3}	1×10^{-2}	5×10^{-1}	1×10^{-2}	5×10^{-1}	3×10^{-6}	2×10^{-4}	> 99.99	> 99.97
F	1.1×10^{-3}	2.4×10^{-4}[g]	1.3×10^{-3}[g]	4.6×10^{-3}	6×10^{-2}[g]	6×10^{-2}[g]	4.7×10^{-7}	1.9×10^{-6}	> 99.99[g]	> 99.99[g]
G	1.1×10^{-3}	9×10^{-3}[g]	1.0×10^{-2}[g]	3.0×10^{-3}	5×10^{-2}[g]	6×10^{-2}[g]	4.8×10^{-7}	1.3×10^{-6}	> 99.99[g]	> 99.99[g]

---

[a] Actual picloram content of the ~ 10% pellet formulation.

[b] Picloram plus all other chlorinated organic species detected.

[c] Efficiency is defined as $\left[1 - \frac{\text{quantity } \underline{\text{out}}}{\text{quantity } \underline{\text{in}}}\right] \times 100$, where the quantity out is evaluated at Sample Points Nos. ② (the incinerator off-gas) and ③ (solid residues) and the quantity in is evaluated at Sample Point No. ① (the incinerator feed). Efficiencies have been calculated based on (a) picloram only and (b) the total chlorinated organic species detected at Sample Points Nos. ② and ③.

[d] These values for contained picloram are based on the average content (as determined from Runs Nos. A through E) of 7.4%. Triplicate analysis of the feed material for the two additional tests (Runs Nos. F and G, which were from a different production batch than the initial five tests), showed a picloram content of 0.4%. Other picloram analyses for Runs Nos. F and G, however, as shown in Table B-III-6, are comparable to earlier test results. Thus, the value of 7.4% has also been used to calculate the picloram content of the feed for Tests F and G.

[e] No analysis.

[f] Picloram was not detected in all components (i.e., impingers) of the sampling train. The value given includes the detection limit for picloram in these respective elements.

[g] Does not include the quantity present in the solid residue from the second chamber.

Table 48. OFF-GAS COMPOSITION--10% PICLORAM PELLET INCINERATION[a]

						Total hydrocarbons analyzer			Orsat analyzer			
Run No.	Picloram mg/m^3	Total species[c] mg/m^3	CN^- mg/m^3	SO_2 mg/m^3	NO_x[e] mg/m^3	Total hydrocarbons ppm	CO ppm	CH_4 ppm	O_2 vol. %	CO_2 vol. %	CO vol. %	Moisture vol. %
A	$< 1.4 \times 10^{-4}$[b]	$< 8.6 \times 10^{-3}$	NA[d]	NA	NA	304	37	1	10.6	7.7	0.0	8.2
B	$< 4.7 \times 10^{-4}$[b]	9.9×10^{-2}	< 1	NA	NA	46	20	7	13.5	5.5	0.0	3.0
C	$< 5.6 \times 10^{-4}$[b]	2.2	178	NA	NA	52	262	3	14.8	4.6	0.0	9.1
D	$< 7.4 \times 10^{-4}$[b]	3.9	278	NA	NA	53	4,360	2	14.7	4.8	0.0	10.2
E	7.0×10^{-2}	4.4	NA	NA	NA	740	4,010	> 1,040[f]	9.4	8.0	0.8	10.1
F	4.7×10^{-3}	2.0×10^{-2}	< 1	234	59	4	16	ND	9.2	9.2	0.0	8.6
G	3.3×10^{-3}	9.0×10^{-3}	4	127	21	8	ND[g]	ND	12.6	6.4	0.0	7.2

---

[a] As dry gas at one atmosphere pressure, and 21.1°C (70°F).

[b] Picloram was not detected in all components (i.e., impingers) of the sampling train. The value given includes the detection limit for picloram in these respective elements.

[c] Picloram plus all other chlorinated hydrocarbon species detected.

[d] No analysis.

[e] Calculated as NO_2.

[f] Upper detection limit.

[g] Not detected.

Table 49. PARTICULATE SAMPLING SUMMARY--10% PICLORAM PELLET EXPERIMENTS

Description	A	B	C	D	E	F	G
Vol. dry gas - std. cond., nm^3	1.034	0.511	0.215	0.203	0.202	0.398	0.516
Percent moisture by vol.	8.2	3.0	9.1	10.2	10.1	8.6	7.2
Avg. stack temperature, °C	316.0	334.0	177.8	176.6	260.0	303.0	351.2
Stk. flow rate, dry., std. cn., nm^3/min	6.8	5.0	2.0	1.9	2.1	3.8	5.6
Actual stack flow rate, m^3/min	15.5	10.6	3.3	3.2	4.2	8.2	12.8
Percent isokinetic	92.8	97.6	105.1	102.4	100.7	99.2	88.4
Percent excess air	95	172	229	231	71	75	147
Particulates - partial catch							
Particulate wt. - partial, mg	201	203	198	577	2,680	800	285
Part. load - ptl., std. cn., mg/nm^3	194	397	920	2,840	13,300	2,000	551
Part. load - ptl., stk. cn., mg/m^3	85	188	551	1,680	6,540	939	240
Partic. emis. - partial, kg/hr	0.079	0.119	0.108	0.322	1.665	0.464	0.185
Particulates - total catch							
Particulate wt. - total, mg	237	248	242	632	2,710	843	442
Part. load - ttl., std. cn., mg/nm^3	229	484	1,120	3,110	13,400	2,110	855
Part. load - ttl., std. cn., corrected to 12% CO_2, mg/nm^3	357	1,060	2,900	7,800	20,100	2,750	1,600
Part. load - ttl., stk. cn., mg/m^3	101	229	672	1,840	6,590	990	372
Partic. emis. - total, kg/hr	0.094	0.145	0.132	0.353	1.680	0.489	0.288
Percent impinger catch	15.32	18.12	18.07	8.71	0.89	5.13	35.53

Table 50. OPERATIONAL DATA SUMMARY--10% PICLORAM PELLET EXPERIMENTS

Run No.	A	B	C	D	E	F	G
Temperature °C (°F)							
Primary chamber (Thermocouple No. ①)	1000 (1840)	900 (1660)	640 (1190)	710 (1310)	920 (1680)	900 (1660)	830 (1520)
Primary chamber (Thermocouple No. ②)	1020 (1860)	920 (1680)	530 (990)	520 (970)	900 (1650)	850 (1570)	770 (1410)
Primary chamber (Thermocouple No. ③)	1020 (1870)	930 (1710)	600 (1120)	630 (1160)	930 (1700)	950 (1750)	920 (1680)
Second chamber (Thermocouple No. ④)	840 (1550)	800 (1480)	500 (930)	530 (980)	790 (1450)	810 (1490)	830 (1520)
Second chamber (Thermocouple No. ⑤)	500 (930)	520 (960)	250 (490)	280 (530)	450 (850)	580 (1070)	620 (1140)
Sample Point No. ② (Thermocouple No. ⑥)	340 (650)	370 (690)	180 (360)	190 (370)	180 (360)	260 (500)	420 (780)
Pressures							
Draft (Manometer No. △1), pascals (in. H_2O) gauge	21 (0.085)	35 (0.140)	12 (0.050)	12 (0.050)	14 (0.55)	31 (0.125)	54 (0.215)
Burner operation pressure, pascals (psi) gauge	NA[a]	NA	NA	NA	NA	7.4×10^5 (108)	7.4×10^5 (108)
Pesticide injection air, pascals (psi) gauge	6×10^4 (9)	7×10^4 (10)	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	7×10^4 (10)

---

a/ No analysis, gauge broken.

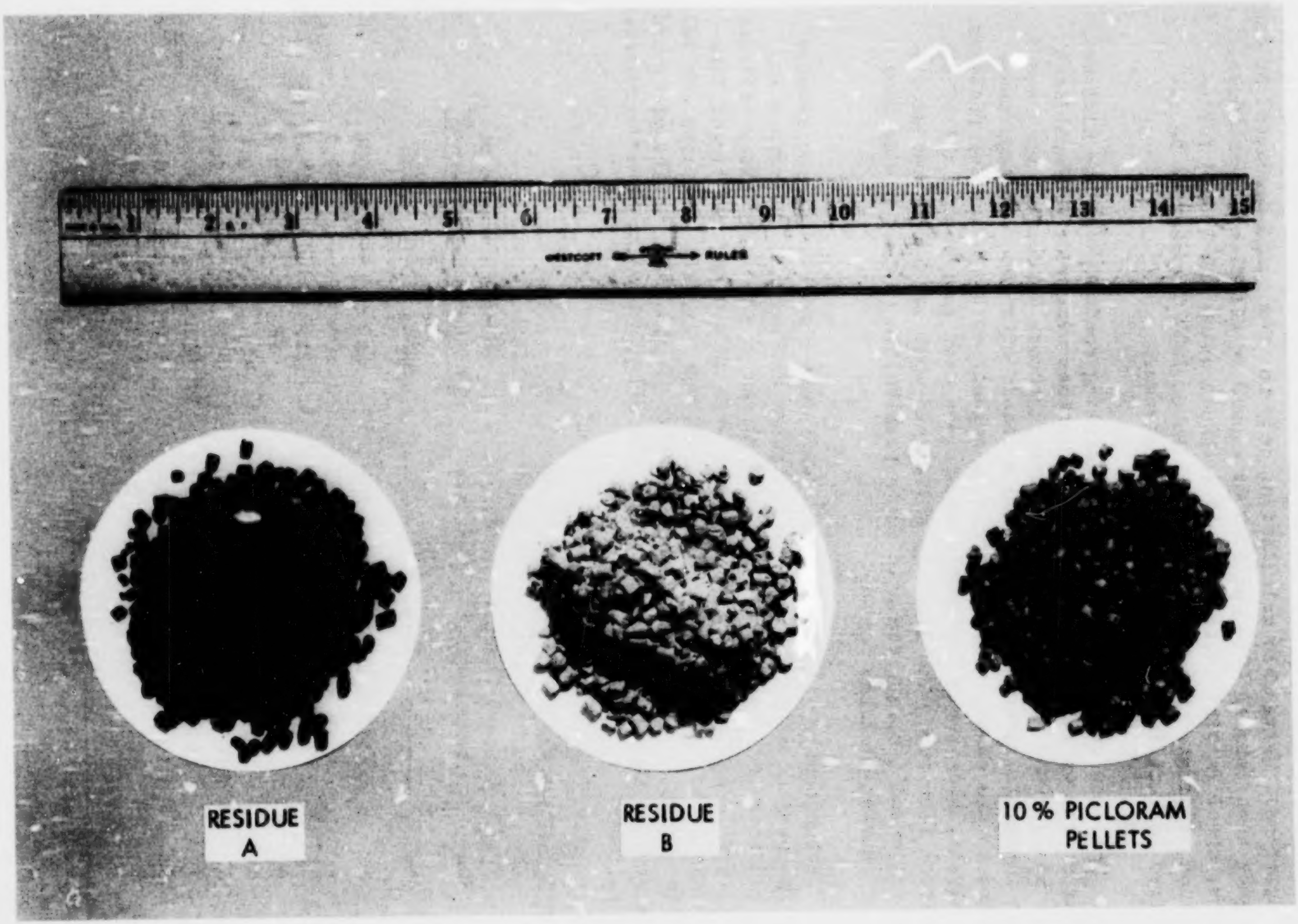


Figure 31. Picloram pellets and residue.

The second efficiency calculation includes not only the picloram that is left, but also other chemical species (volatile chlorinated hydrocarbons). Using this calculation, only the two tests conducted at the higher temperatures (930 and 1020°C) showed an efficiency of > 99.99%. Thus, these initial tests, as well as those using the liquid formulation, indicate that temperatures of about 1000°C appear to be required to satisfactorily incinerate picloram.

The results of the particulate sampling conducted on the picloram runs are shown in Table 49. Two modifications were made to facilitate the analysis of the sample for picloram content; 2-propanol was used in the impingers rather than water and a liquid nitrogen cold trap was added to the sample train in order to collect condensibles for picloram analysis. Acceptable isokinetic conditions were achieved in all of the initial five runs. The loadings all exceed what can be considered low emission and indicate the need for a particulate control device when incinerating picloram pellets.

Subsequently, four additional tests were conducted at the request of the project officers in order to better define the temperature required to reduce cyanide (CN^-) concentration in the incinerator effluent gas to < 1 mg/m^3. Two additional tests were made using the liquid formulation (Runs Nos. 8 and 9, Tables 42 through 45), and two using the 10% pellets (Runs Nos. F and G, Tables 46 through 50). The results of cyanide analysis of the incinerator effluent for all picloram tests are summarized as follows:

Liquid formulation

Run No.	Primary chamber temperature °C (°F)	Excess air %	Cyanide content of incineration off-gas[a] mg/m^3	Cyanide content of incineration off-gas[a] g/hr
1	530 (990)	298	689	79.9
2	600 (1120)	193	906	99.7
3	630 (1160)	187	211	23.8
4	930 (1700)	62	98	14.7
5	1010 (1850)	130	< 1	< 0.4
6	1030 (1880)	116	< 1	< 0.4
7	800 (1470)	77	967	104.4
8	1000 (1840)	114	< 1	< 0.3
9	1010 (1850)	50	2	0.4

---

a/ Calculated as CN^-.

Pellet formulation

A	1020 (1870)	93	NA[b]	NA
B	930 (1710)	170	< 1	< 0.3
C	640 (1190)	226	178	21.2
D	710 (1310)	227	278	31.4
E	930 (1700)	72	NA	NA
F	950 (1750)	75	< 1	< 0.2
G	920 (1680)	145	4	1.3

---

[b] No analyses.

For the liquid formulation tests, only those experiments conducted in the higher temperature ranges, 1000 to 1030°C (1840 to 1880°F), produced low concentrations (and quantities) of cyanide in the off-gas. Low concentrations (< 1 mg/m^3) and quantities of cyanide were generally also produced from the pellet formulation tests conducted at the higher temperature, 930 and 950°C (1710 and 1750°F). Thus, these data indicate that a temperature of about 1000°C and sufficient excess air (~ 100%) are required to minimize cyanide generation.

Additional samples were also taken during the supplemental pellet formulation experiments (Runs Nos. F and G, Tables 46 through 50), using a special sampler installed in the bottom of the primary combustion chamber (see Figure 32). This sampler was used to "catch" pellets as they fell through the combustion chamber in order to approximate the degree of decomposition actually occurring while the pellet was falling. The sampler was inserted upside down, rotated, and immediately (~ 3 sec) extracted to obtain grab sample with a nominal retention time in the primary combustion chamber of about 2 sec. The grab samples (two and three per run, respectively) were analyzed for the picloram content, and gave the following results:

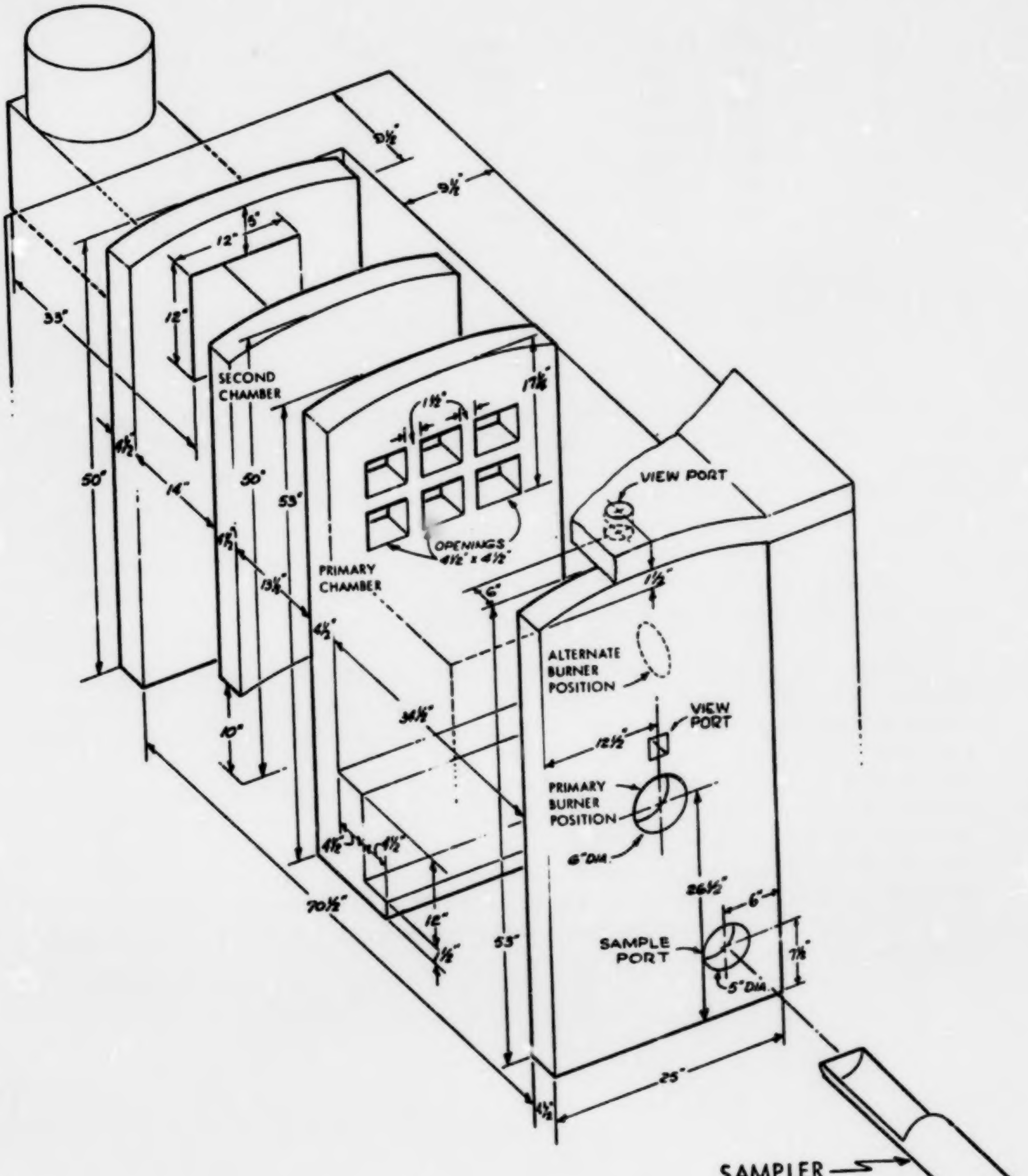


Figure 32. Primary chamber residue sampler

	Picloram ppm	Total species[a/] ppm
Run No. F		
Primary chamber residue composition	0.01	2.5
Average "grab" sample composition	124	1,041
Run No. G		
Primary chamber residue composition	0.4	1.9
Average "grab" sample composition	65.3	265

[a/] Picloram plus all other chlorinated organic species detected.

These values when compared to the nominal picloram content of the feed (~ 74,000 ppm) indicate that the vast majority of the picloram (as well as the other chlorinated species) are "removed" from the pellet during the first 2 sec residence time in the primary chamber.

DISCUSSION

Several minor operational problems were encountered during the incineration of picloram. The first of these, as alluded to earlier, was the pumping of the water-based liquid picloram formulation. This material would neither stay in suspension as a fuel oil mixture, nor be successfully pumped through a system designed to handle only hydrocarbons. This problem was overcome by injecting the undiluted picloram formulation through a separate injection system consisting of a gear pump designed to handle aqueous systems and a standard burner nozzle of the appropriate size

The incineration of picloram in both the liquid and the pellet formulation can be classified as giving relatively dirty burns. A dark (bluish) exhaust plume was discharged from the experimental system (i.e., at Sample Point No. ⑨ , Figure 5, p. 27) during most of the tests.

The dirtiness of the burns caused minor plugging problems with the demister pad in the first stage water scrubber. This problem was particularly noticable when operating the incinerator at low draft (see Table 50).

References

1. Lawless, E. W., T. L. Ferguson, and A. Meiners, "Guidelines for the Disposal of Small Quantities of Unused or Spilled Pesticides" (Draft), EPA Contract No. 68-01-0098 (1974).

2. Lawless, E. W., R. von Rümker, and T. L. Ferguson, "The Pollution Potential in Pesticide Manufacturing," EPA Technical Studies Report No. TS-00-72-04 (June 1972).

3. Kennedy, M. V., B. J. Stojanovic, and F. L. Shuman, Jr., "Chemical and Thermal Methods for Disposal of Pesticides," *Res. Rev.*, **29**:89 (1969).

4. Li, R., and E. C. Lim, *J. Chem. Phys.*, **57**(2):605 (1972).

5. Zweidinger, R., and J. D. Winfordner, *Anal. Chem.*, **42**(6):639 (1970).

6. *Herbicide Handbook of the Weed Science Society of America*, 2nd ed., W. F. Humphrey Press, Inc., Geneva, New York (1970).

IV. MALATHION

PESTICIDE DESCRIPTION

Physical Properties

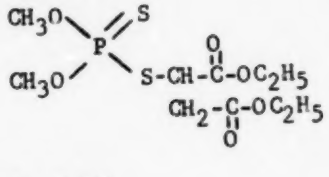
Chemical Name: S-[1,2-bis(ethoxycarbonyl)ethyl]O,O-dimethyl phosphorodithioate; O,O-dimethyl phosphorodithioate of diethylmercaptosuccinate

Common Name: Malathion

Trade Names: Cythion®, Emmatos®, Emmatos Extra®, Fyfanon®, Karbofos®, Kop-Thion®, Kypfos®, Malaspray®, Malamar®, MLT, Zithiol®, Mercaptothion®, Carbofos®, Maldison®

Pesticide Class: Nonsystemic insecticide and acaricide; organophosphate

Structural Formula:



Empirical Formula: $C_{10}H_{19}O_6PS_2$

Molecular Weight: 330.36

Analysis: C 36.35%; H 5.80%; P 9.38%; S 19.41%; O 29.06%

Physical State: Clear liquid, may be colorless, yellow, amber or brown

Characteristics: Technical grade material is a minimum 95% purity. It has a slight characteristic mercaptan-like odor, but has a maximum 30 ppm methyl mercaptan. Malathion insecticide concentrates may gel if stored in contact with iron, terneplate, or tin plate for a prolonged period. No gelation has been observed in finished malathion insecticide aerosols or other formulations containing 5% or less of the insecticide. Malathion insecticide concentrates may solidify if stored at temperatures ranging around 0°C (32°F); the product will increase in viscosity. Normal viscosity can be restored by allowing drums of malathion to warm up to 4.5° C(40°F). (Cyanamid International undated).1/

Melting Point: 2.85°C

Boiling Point: 156 to 157°C at 0.7 mm Hg (slight decomposition)

Vapor Pressure: 0.00004 mm Hg at 30°C

Specific Gravity: 1.2315 at 25°C

Density: 1.2 kg/liter (10.25 lb/gal)

Refractive Index: n_D^{25} 1.4985

Viscosity: At 40°C, 0.176 dyne/sec/cm^2 (17.57 centipoises)
At 25°C, 0.368 dyne/sec/cm^2 (36.78 centipoises)

Flash Point (Tag Open Cup): Greater than 160°C (320°F)

Solubility: In water at 25°C, approximately 145 ppm. Completely soluble in most alcohols, esters, high aromatic solvents, ketones and vegetable oils. Poor solubility in aliphatic hydrocarbons.

Chemical Properties

Hydrolysis is the most important decomposition reaction of malathion and has received intense investigation. Depending upon the reaction conditions, hydrolysis can occur via several different pathways leading to a variety of products. The thermal decomposition of malathion has also been investigated, but relatively little is known concerning the decomposition products. Malathion is readily oxidized to malaoxon, a reaction typical of other sulfur-containing organophosphate pesticides. Malathion is degraded by ultraviolet radiation, but little is known concerning this reaction. The chemical reactions of malathion are described in the following paragraphs.

Malathion is a reasonably stable compound that undergoes some decomposition when held much above room temperature. Heating the purified, nearly colorless liquid for 24 hr at 150°C resulted in the formation of an orange-brown, viscous liquid and some colorless cloudy material which was immiscible (Metcalf and March).[2] This treatment resulted in the isomerization of approximately 90% of the original material. No decomposition products were identified.

McPherson and Johnson[3] examined the variation of decomposition time with temperature and, for malathion, obtained the following results.

Temperature (°C)	Decomposition time (days)
115	5
100	20
80	163
65	925

The burning of malathion solutions was investigated by Smith and Ledbetter.[4] Malathion solutions (1 g/10 ml) in xylene and kerosene were burned and gases collected above the fire were analyzed. Samples were collected at various intervals after the ignition of the solutions. The maximum malathion found from the burning malathion-xylene solutions was 10 $\mu g/m^3$ at 4.5 min after ignition, and that from the kerosene mixture was 4 $\mu g/m^3$ at 2.5 min. Smith and Ledbetter noted that these quite low concentrations could result from either a high efficiency of combustion or a failure of the malathion to evaporate during the burning.

Some of the decomposition products of malathion were identified during the experiments. Diethyl fumarate was separated and positively identified by infrared spectrophotometry. Some other compounds were tentatively identified by their retention times in gas chromatography. Compounds tentatively identified by Smith and Ledbetter were:

Methanol

Ethanol

Ethyl acetate

Diethyl fumarate

Isomers of dimethyl dithiophosphate

Malathion isomers

Smith and Ledbetter[4] concluded that several factors tend to reduce the hazards from organophosphate (e.g., malathion) insecticides in fires. First, most of the pesticide is destroyed by decomposition before it can evaporate. Second, over 90% of the evaporating insecticide is destroyed by the flames. Third, the evaporating portion is considerably diluted by the time it reaches anyone.

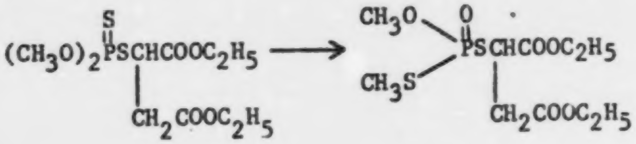
Differential thermal analysis of malathion by Kennedy et al.[5] provided the following data.

Product	Endotherms	Exotherms
Reference standard	500°C	250, 308, 333, and 422°C
Commercial product (5 lb/gal)	145, 441, and 475°C	261 and 308°C

Sensitivity = 25%.

Based on these and other laboratory analyses, Kennedy et al. concluded that the temperature of complete combustion of the malathion reference standard and the 57% liquid formulation were 663°C (1225°F) and 715°C (1319°F), respectively.

According to Melnikov,[6] malathion, on prolonged heating at 150°C, is isomerized to the corresponding thiolo isomer:



$$(CH_3O)_2\overset{\overset{S}{\|}}{P}S\underset{\underset{CH_2COOC_2H_5}{|}}{CH}COOC_2H_5 \longrightarrow \begin{matrix} CH_3O \\ CH_3S \end{matrix}\!\!>\overset{\overset{O}{\|}}{P}S\underset{\underset{CH_2COOC_2H_5}{|}}{CH}COOC_2H_5$$

At a higher temperature, this reaction proceeds violently and a considerable amount of the product is decomposed, sometimes even explosively.

The thermal decomposition of a commercial malathion formulation (5 lb/gal) at various temperatures was also investigated by Kennedy et al.[5] Extensive decomposition would have been expected at the high temperatures reported; thus the contact time, which was not reported, must have been very short, or the reported loss was equivalent to total decomposition. The results from this study are summarized as follows.

Temperature (°C)	Percent loss
600	95.3
700	96.0
800	96.3
900	96.4
1000	96.7

Kennedy et al.[5] further investigated the thermal decomposition of malathion (analytical grade). The observed effects of heating on weight loss, color and physical appearance were as follows.

Heating time (min)	Temperature (°C)	Weight loss (%)	Color	Physical appearance
30	200	58.7	Dark-brown	Liquid
30	250	72.9	Dark-brown	Liquid, jelly-like on cooling
30	300	76.2	Dark-brown	Silk flakes
30	350	80.3	Dark-brown	Silk flakes
30	400	80.3	Dark-brown	Silk flakes
30	500	80.3	Dark-brown	Silk flakes
30	600	80.3	Dark-brown	Silk flakes

Additional data on the decomposition of malathion were reported by Stojanovic et al.[7] In general, the same physical changes previously reported were observed when malathion was heated. Diethyl succinate, diethyl malate and diethyl fumarate were tentatively identified as decomposition products on the basis of infrared spectra.

In another study of pesticide combustion (Putnam et al.),[8] it was reported that malathion decomposed over the temperature range of 277 to 326°C.

Production and Use

Malathion has a very broad spectrum of effectiveness against insects and mites. It is registered and recommended in the United States for use on about 130 different crops, on livestock and pets, and on agricultural premises such as barns (including dairy barns and milk rooms), feedlots, holding pens, poultry houses, feed rooms, and grain bins. The foregoing count of 130 crops includes several dozen minor vegetables counted as only one crop. Tolerances for malathion residues have been established on at least 127 raw agricultural commodities (EPA).[9]

It is estimated that about 16.2 million pounds of malathion (as active ingredient) were used in the United States in 1972.[10] Consumption of malathion by category of use in 1972 is estimated to have been: agriculture - 5 million pounds; industrial and commercial uses - 4 million pounds; government agencies - 2.2 million pounds; and home and garden uses - 5 million pounds.

Malathion is available to users in the United States in a variety of different formulations including emulsifiable liquids, wettable powders, dusts, solutions, concentrates for low volume (LV) and ultra-low volume (ULV) applications, and manufacturing concentrates.

FORMULATIONS TESTED

Two malathion formulations were tested: a 57% emulsifiable concentrate; and a 25% wettable powder. The available information on these formulations is summarized as follows.

57% Emulsifiable Concentrate

Name: Crown Malathion 57%

Manufacturer: Crown Chemicals, Rockford, Illinois

Composition: Active Ingredients

Malathion*	57.00%
Aromatic Petroleum Derived Solvent	33.09%
Inert Ingredients	9.91%
Total	100.00%

---

* O,O-dimethyl dithiophosphate of diethyl mercaptosuccinate

Registration: EPA Reg. No. 7273-59

Lot No.: 16646

25% Wettable Powder

Name: Niagara Malathion 25 Wettable

Manufacturer: Niagara Chemical Division, FMC Corporation,
Middleport, New York

Composition: Active Ingredients

Malathion*	25.0%
Inert Ingredients	75.0%
Total	100.0%

---

* O,O-dimethyl dithiophosphate of diethyl mercaptosuccnate

Registration: USDA Reg. No. 279-761

Lot No.: A650 AY, A650 PX, M6524 ET

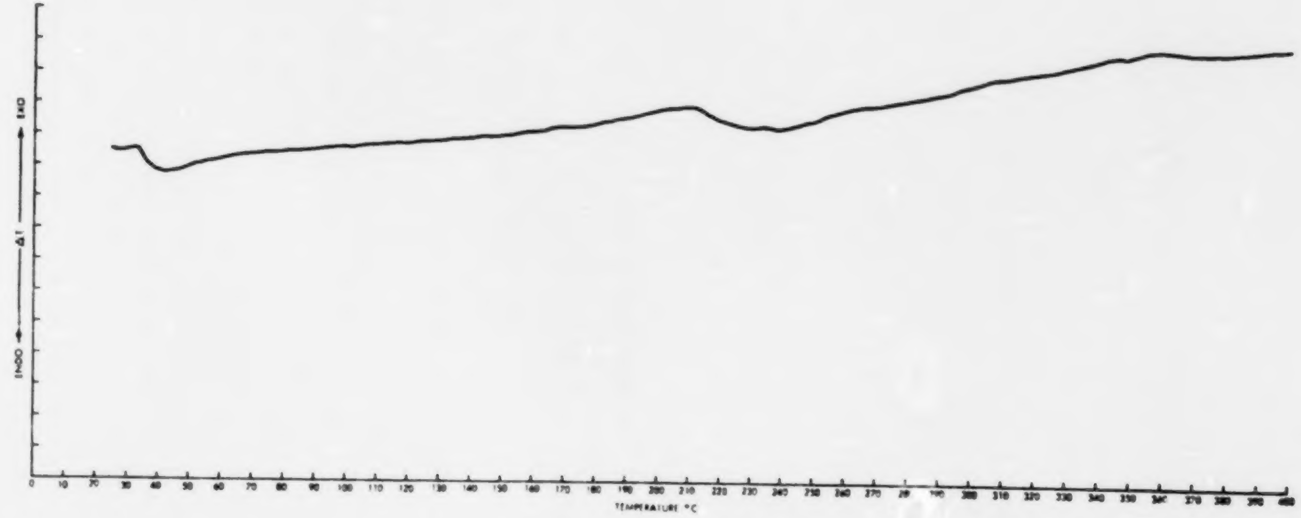
Particle Size Specifications: At least 99% pass through a 44 µ (325 mesh) sieve.

PRELIMINARY THERMAL ANALYSIS

Bomb calorimetric analyses of the two formulations gave the following:

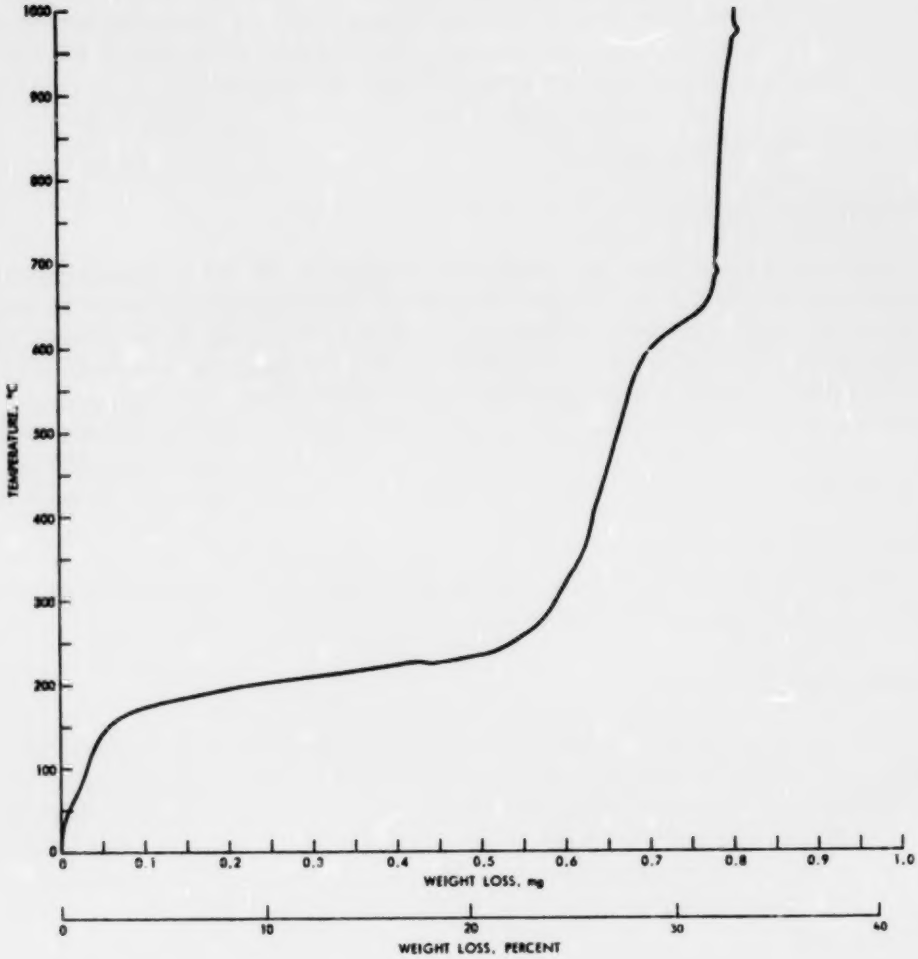
Sample	Test	Test Method	Result
25% Malathion powder formulation	Sulfur	ASTM D-1552	5.21%
	Calorific value	ASTM D-240	5.510×10^6 J/kg (2,371 Btu/lb)
57% Malathion liquid formulation	Sulfur	ASTM D-1552	11.57%
	Calorific value	ASTM D-240	2.793×10^7 J/kg (12,017 Btu/lb)

Figures 33 and 34 show the results of DTA and TGA of the 25% malathion powder formulation. The DTA data do not show any prominent exotherms or endotherms. Rather, a slow decomposition process is indicated. Such a process is substantiated by the TGA data that indicate slow weight loss as temperature increases. At about 650°C almost 30% of the original weight is gone; nominal malathion content of the formulation is 25%. Essentially no more weight loss is observed from 650 to 1000°C.



Reference: Empty pan
Prog. mode: Heat
Rate: 10°C/min
Start: 24°C

Figure 33. DTA of malathion powder



Sample weight: 2.434 mg
Heating rate: 20°C/min
Environment: ~ 20 ml/min air (20% O_2, 80% N_2)

Figure 34. TGA of malathion powder

Figures 35 and 36 show the results of DTA and TGA of a sample of malathion obtained by evaporation of a sample of the 57% EC formulation. DTA data show no prominent exotherms or endotherms. However, a marked decomposition process occurs from about 338°C and on to the instrument limit of 400°C. This decomposition process is substantiated by the slow weight loss observed on the TGA data (Figure 36) as temperature increases. At about 700°C, almost 80% of the original weight is gone. From 700 to 1000°C, another 10% of the original weight disappears.

METHODS OF ANALYSIS

Apparatus

For gas chromatographic analysis a Tracor 550 gas chromatograph equipped with FPD 200 AT sulfur and phosphorus flame photometric detectors (Meloy, Inc., Springfield, Virginia) and a 6-ft, 4 mm I.D. glass column (packed with 1.5% OV-17 + 1.95% QF-1 on 80/100 mesh Supelcoport from Supelco, Inc., Bellefonte, Pennsylvania) were used. Chromatographic operating conditions were: injector temperature, 240°C; column temperature, 200°C; detector temperature, 235°C; carrier flow rate, 100 ml/min, N_2; detector flow rate, 30 ml/min, O_2; 175 ml/min, H_2; and 34 ml/min, air.

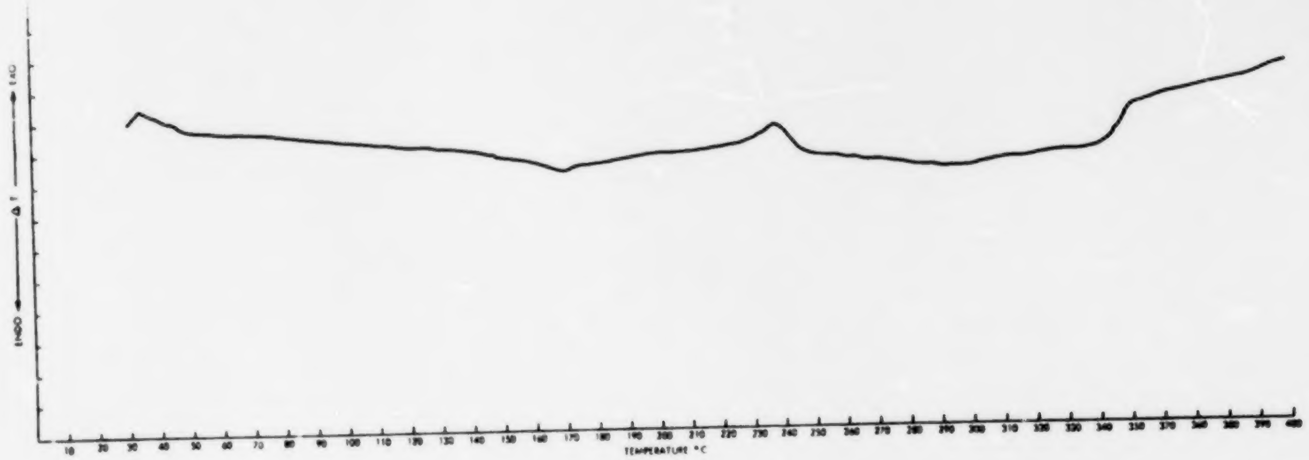
A Tracor Westronics Model MT 22 dual pen strip chart recorder was used to record the chromatograms.

Reagents and Materials

Solvents used were pesticide grade benzene (Fisher Scientific) for extraction of water samples and for standard solutions, and pesticide grade hexane (Matheson, Coleman, Bell) for extraction of hexylene glycol (second stage scrubber samples). All laboratory glassware was thoroughly rinsed in dilute hydrochloric acid (Fisher Scientific), deionized distilled water and reagent grade acetone (Fisher Scientific).

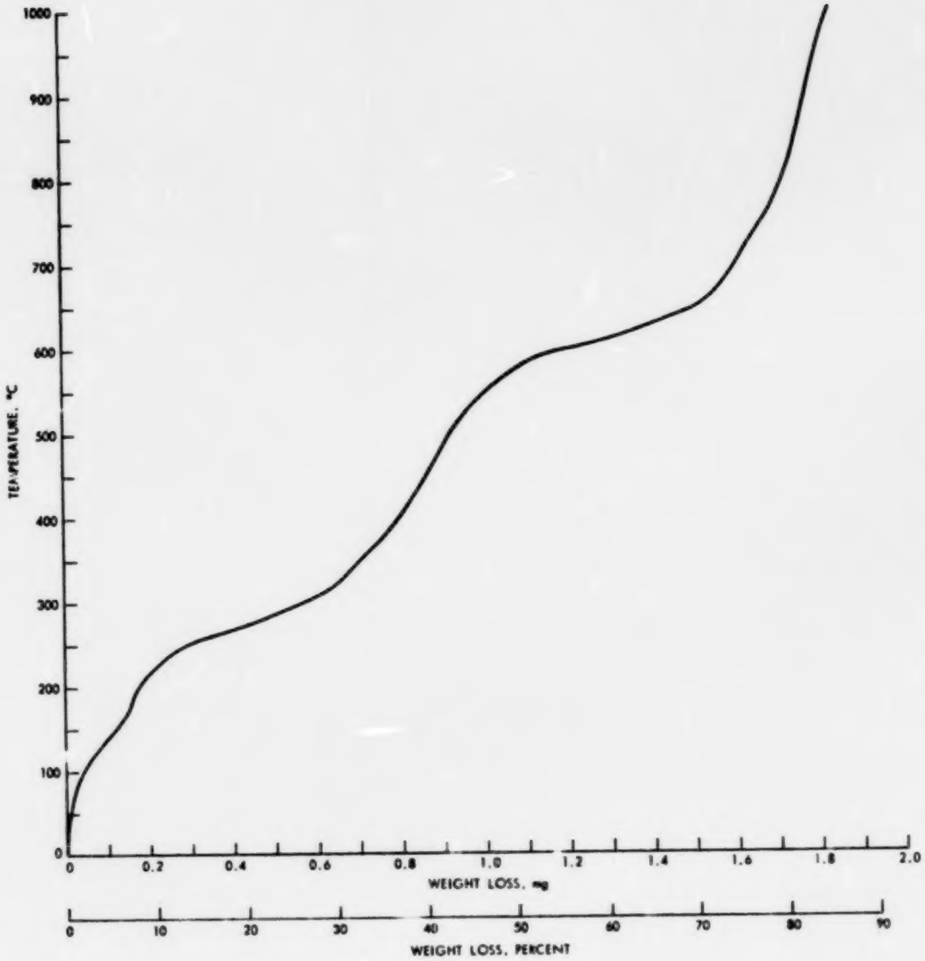
Standard and Calibration Curves

The solid malathion standard obtained from EPA, was used to prepare a stock standard of 100 μg/ml and appropriate dilutions were made to produce a linear curve (linear range used: 0 to 50 ng).



Reference: Glass beads
Prog. mode: Heat
Rate: 10°C/min
Start: 30°C

Figure 35. DTA of malathion



Sample weight: 2.15/mg
Heating rate: 20°C/min
Environment: ~20 ml/min water pumped air

Figure 36. TGA of malathion

Procedure for Sample Preparation

All samples collected in water were extracted with 10 ml benzene (includes samples in dilute sulfuric acid) and appropriate amounts (2 to 5 µl) were injected into the G.C. On all other samples (which were collected in acetone or benzene) the volumes were measured and appropriate amounts were injected into the G.C. Twenty milliliters of the hexylene glycol samples (from second stage scrubber) were extracted with two 5 ml portions of hexane, and appropriate amounts of the hexane extracts were injected for analysis. The volume of liquid in the N_2 cold trap and the glass wool plug in the trap were each extracted with 10 ml of benzene and a portion of this extract was analyzed for malathion. Filter elements from all gas sample points were extracted with two 5 ml portions of benzene and the benzene extract analyzed for malathion.

The mass of collected particulates was determined for all samples collected from incineration of malathion dust as follows. All samples of impinger solutions were evaporated in clean, dessicated, tared 250 ml beakers and dessicated 2 days before final weighing. The residues were extracted (using an ultrasonic mixer) with known volume of benzene and portions of the extracts were analyzed by G.C. The cold trap solutions were extracted with two 5 ml portions of benzene and the benzene extract analyzed. Blank acetone and benzene samples were analyzed as received. The silica gel was extracted with a known volume of benzene and an appropriate amount was injected for analysis.

Portions of all solid residue samples (from the primary chamber, secondary chamber, etc.) were weighed out, extracted, and the extracts were analyzed for malathion.

Analysis and Discussion

All samples were analyzed for malathion. Unidentified chromatographic peaks were quantitated against the phosphorus response of standard malathion.

The sensitivity of the instrument for malathion is 1 ng. Based on this sensitivity value and with a 5 µl sample injection for each analysis, the minimum detectable quantity for a 20 ml sample solution is 4 µg. However, during the analysis, samples were very often concentrated down to 1 ml which resulted in a minimum detectable quantity of 0.02 µg.

The detection limit for each sample point as reported in the following subsection on "Test Conditions and Results," is dependent on not only the sensitivity of the instrument as has been outlined, but also on the size of the sample analyzed, e.g., the volume of incinerator off-gas drawn through the sampling train, or the size of the solid residue extracted. The detection limits reported in the following, therefore represent the limits for detection in the specific samples analyzed and vary from test to test.

TEST CONDITIONS AND RESULTS

A total of 11 tests were conducted using the 57% malathion emulsifiable concentrate (EC) formulation. The results of these tests are summarized in Tables 51 through 54.

Initially, nine tests were made using the EC formulation (Runs Nos. 1 through 9). Neither malathion nor any other sulfur-containing organic phosphates were detected at Sample Point No. ②(the incinerator off-gas) for any of these experiments. Further, neither malathion nor any other sulfur-containing phosphates were detected at any other point in the experimental system except at Sample Point No. ① (the incinerator feed).

Relatively high quantities of total pyrophosphates, however, were detected in the incinerator effluent from those runs using concentrated feed (350 to 590 mg malathion per milliliter) (Runs Nos. 5 through 9).

Two additional tests (Runs Nos. 10 and 11) were then made using lower concentrations of malathion. As had been the case with Runs Nos. 1 through 9, no malathion was detected in the incinerator effluent. Runs Nos. 10 and 11, however, failed to parallel earlier results in which detectable levels of total pyrophosphates were found only in tests where relatively high concentrations of malathion (350 to 590 mg/ml) were burned. Thus, a definite correlation could not be made between pyrophosphate generation and either operating temperature or incinerator feed concentration.

Table 51. SUMMARY OF 57% MALATHION EC EXPERIMENTS

Run No.	Incinerator feed rate: Nominal burner size ℓ/hr (gal/hr)	Incinerator feed rate: Total feed rate ℓ/hr (gal/hr)	Incinerator feed rate: Malathion rate g/hr (lb/hr)[a]	Incinerator feed rate: Malathion rate ℓ/hr (gal/hr)[b]	Incinerator feed rate: Malathion concentrate mg/ml	Incinerator feed rate: No. 2 Fuel oil rate ℓ/hr (gal/hr)	Primary chamber temperature °C (°F)	Flame temperature[c] °C (°F)	Excess air[d] %	Retention time[e] sec: Primary chamber	Retention time[e] sec: Second chamber	Sampling time min	Off-gas flow rate[f] m³/hr (1,000's of SCFH)
1	13.2 (3.5)	10.07 (2.66)	1,760 (3.89)	3.60 (0.95)	175	6.47 (1.71)	1050 (1930)	-	130	2.2	2.2	30	249 (8.8)
2	11.4 (3.0)	9.54 (2.52)	2,630 (5.80)	5.34 (1.41)	195	4.20 (1.11)	1060 (1940)	-	74	3.6	3.7	30	139 (4.9)
3	9.5 (2.5)	8.29 (2.19)	1,470 (3.24)	2.99 (0.79)	250	5.30 (1.40)	1000 (1840)	-	44	4.8	5.0	30	110 (3.9)
4	11.4 (3.0)	8.40 (2.22)	930 (2.04)	1.89 (0.50)	110	6.51 (1.72)	1080 (1980)	1210 (2210)	122	2.2	2.6	30	224 (7.9)
5	3.8 (1.0)	3.33 (0.88)	1,170 (2.58)	2.38 (0.63)	350	0.95 (0.25)	620 (1140)	1100 (2010)	176	6.8	6.5	30	116 (4.1)
6	4.7 (1.25)	3.79 (1.00)	1,970 (4.35)	3.79 (1.00)	590	0	640 (1190)	1120 (2040)	188	6.6	6.5	30	110 (3.9)
7	5.1 (1.25)	4.31 (1.14)	1,990 (4.38)	4.31 (1.14)	460	0	690 (1270)	1070 (1950)	114	6.2	6.2	30	110 (3.9)
8	4.7 (1.25)	3.75 (0.99)	1,640 (3.62)	3.10 (0.82)	440	0.64 (0.17)	700 (1290)	1120 (2040)	114	6.0	6.1	30	119 (4.2)
9	11.4 (3.0)	7.27 (1.92)	3,630 (8.00)	6.74 (1.78)	500	0.53 (0.14)	960 (1760)	1150 (2110)	95	3.9	3.9	30	150 (5.3)
10	3.8 (1.0)	3.56 (0.94)	660 (1.45)	1.32 (0.35)	185	4.16 (1.10)	620 (1150)	-	197	5.1	5.1	30	161 (5.7)
11	3.8 (1.0)	3.26 (0.86)	630 (1.39)	1.25 (0.33)	195	4.01 (1.06)	600 (1110)	-	311	4.6	4.3	30	184 (6.5)

---

a/ Actual malathion content of the incinerator feed.
b/ Volume of the ~ 57% formulation per hour.
c/ The flame temperature was observed at a point ~ 15 cm (6 in.) in from the front wall of the incinerator.
d/ Calculated according to Method 3 of "Standards of Performance for New Stationary Sources," *Federal Register*, 36(247):24876-24895, 23 December 1971).
e/ Retention time is defined as $\frac{V}{v}$, where v is the wet off-gas flow rate from the incinerator at the respective chamber temperature and pressure, and V is the volume of that chamber.
f/ As dry gas at one atmosphere pressure, and 21.1°C (70°F).

Table 52. INCINERATION EFFICIENCY--57% MALATHION EC EXPERIMENTS

Run No.	Malathion feed rate[a] g/hr	Malathion content of off-gas[b] g/hr	Total species[c] content of off-gas g/hr	Ratio of malathion in the off-gas[b] to malathion fed	Ratio of total species[c] content of the off-gas to to malathion fed	Incinerator efficiency[d] % Malathion	Incinerator efficiency[d] % Total species[c]
1	1,760	$< 3.3 \times 10^{-2}$	$< 1.0 \times 10^{-1}$	$< 1.9 \times 10^{-5}$	$< 6 \times 10^{-5}$	> 99.99	> 99.99
2	2,630	$< 1 \times 10^{-2}$	$< 7 \times 10^{-2}$	$< 5 \times 10^{-6}$	$< 3 \times 10^{-5}$	> 99.99	> 99.99
3	1,470	$< 1 \times 10^{-2}$	$< 2 \times 10^{-2}$	$< 8 \times 10^{-6}$	$< 2 \times 10^{-5}$	> 99.99	> 99.99
4	930	$< 2.4 \times 10^{-2}$	$< 4.8 \times 10^{-2}$	$< 2.6 \times 10^{-5}$	$< 5 \times 10^{-5}$	> 99.99	> 99.99
5	1,170	$< 1 \times 10^{-2}$	$< 3 \times 10^{-2}$	$< 1 \times 10^{-5}$	$< 3 \times 10^{-5}$	> 99.99	> 99.99
6	1,970	$< 1 \times 10^{-2}$	$< 3 \times 10^{-2}$	$< 6 \times 10^{-6}$	$< 1 \times 10^{-5}$	> 99.99	> 99.99
7	1,990	$< 1 \times 10^{-2}$	$< 3 \times 10^{-2}$	$< 6 \times 10^{-6}$	$< 1 \times 10^{-5}$	> 99.99	> 99.99
8	1,640	$< 1 \times 10^{-2}$	$< 3 \times 10^{-2}$	$< 8 \times 10^{-6}$	$< 2 \times 10^{-5}$	> 99.99	> 99.99
9	3,630	$< 2 \times 10^{-2}$	$< 3 \times 10^{-2}$	$< 4 \times 10^{-6}$	$< 9 \times 10^{-6}$	> 99.99	> 99.99
10	560	$< 2 \times 10^{-2}$	$< 3 \times 10^{-2}$	$< 3 \times 10^{-5}$	$< 5 \times 10^{-5}$	> 99.99	> 99.99
11	630	$< 2.0 \times 10^{-2}$	$< 4.0 \times 10^{-2}$	$< 3.2 \times 10^{-5}$	$< 6 \times 10^{-5}$	> 99.99	> 99.99

---

a/ Actual malathion content of the incinerator feed.

b/ Malathion was not detected in any effluent gas. The values shown represent the detection limit for each test.

c/ Malathion (its detection limit) plus all other organic phosphate species detected.

d/ Efficiency is defined as $\left[1 - \frac{\text{quantity \underline{out}}}{\text{quantity \underline{in}}}\right] \times 100$, where the quantity out is evaluated at Sample Point No. ② (incinerator off-gas), and the quantity in is evaluated at Sample Point No. ① (the incinerator feed). Efficiencies have been calculated based on: (a) the malathion detection limit only; and (b) malathion plus all other organic phosphate species detected.

Table 53. OFF-GAS COMPOSITION--57% MALATHION EC INCINERATION[a]

					Total hydrocarbons analyzer			Orsat analyzer			
Run No.	Malathion[b] mg/m^3	Total species[c] mg/m^3	SO_2 mg/m^3	NO_x[d] mg/m^3	Total hydrocarbons ppm	CO ppm	CH_4 ppm	O_2 vol. %	CO_2 vol. %	CO vol. %	Moisture vol. %
1	$< 1.3 \times 10^{-1}$	$< 4.0 \times 10^{-1}$	3,430	677	242	2,790	160	12.2	6.5	0.2	0.0
2	$< 1.0 \times 10^{-1}$	$< 4.9 \times 10^{-1}$	8,080	1,050	15	4,380	< 1	9.2	9.1	0.1	10.5
3	$< 1.1 \times 10^{-1}$	$< 2.2 \times 10^{-1}$	5,540	33	27	3,340	23	6.7	10.4	0.1	8.1
4	$< 1.1 \times 10^{-1}$	$< 2.1 \times 10^{-1}$	2,180	35	698	ND	< 1	11.9	6.8	0.1	4.1
5	$< 1.0 \times 10^{-1}$	$< 2.7 \times 10^{-1}$	5,360	23	5	ND	1	13.6	5.6	0.0	5.2
6	$< 1.0 \times 10^{-1}$	$< 2.5 \times 10^{-1}$	7,910	22	3	1	2	13.9	5.3	0.0	8.4
7	$< 1.0 \times 10^{-1}$	$< 2.4 \times 10^{-1}$	8,210	45	18	ND	< 1	11.4	7.4	0.1	9.7
8	$< 1.1 \times 10^{-1}$	$< 2.8 \times 10^{-1}$	5,210	19	ND[e]	ND	< 1	11.5	7.1	0.0	4.6
9	$< 1.0 \times 10^{-1}$	$< 2.3 \times 10^{-1}$	6,050	130	87	ND	< 1	10.6	7.8	0.1	4.3
10	$< 1.1 \times 10^{-1}$	$< 2.1 \times 10^{-1}$	1,580	182	26	< 1	14	14.1	5.1	0.0	5.0
11	$< 1.1 \times 10^{-1}$	$< 2.2 \times 10^{-1}$	631	141	14	ND	7	16.0	3.7	0.1	4.5

---

[a] As dry gas at one atmosphere pressure, and 21.1°C (70°F).

[b] Malathion was not detected in any effluent gas. The values shown represent the detection limit for each test.

[c] Malathion (its detection limit) plus all other organic phosphage species detected.

[d] Calculated as NO_2.

[e] Not detected.

Table 54. OPERATIONAL DATA SUMMARY--57% MALATHION EC EXPERIMENTS

Run No.	1	2	3	4	5	6	7
Temperature °C (°F)							
Primary chamber (Thermocouple No. ①)	1050 (1930)	1070 (1950)	1020 (1860)	990 (1810)	620 (1140)	640 (1190)	680 (1260)
Primary chamber (Thermocouple No. ②)	1030 (1880)	1050 (1930)	1000 (1840)	960 (1760)	560 (1040)	590 (1100)	640 (1180)
Primary chamber (Thermocouple No. ③)	1060 (1940)	1060 (1940)	1000 (1830)	980 (1800)	650 (1200)	680 (1250)	720 (1330)
Second chamber (Thermocouple No. ④)	980 (1800)	900 (1650)	890 (1630)	830 (1530)	580 (1070)	580 (1080)	620 (1140)
Second chamber (Thermocouple No. ⑤)	620 (1150)	610 (1130)	540 (1010)	570 (1060)	380 (720)	370 (700)	390 (740)
Sample Point No. ② (Thermocouple No. ⑥)	350 (660)	310 (590)	230 (450)	330 (630)	170 (330)	180 (350)	170 (340)
Pressures							
Draft (Manometer No. △), pascals (in. H_2O) gauge	22 (0.090)	21 (0.085)	12 (0.050)	35 (0.140)	2 (0.010)	19 (0.075)	19 (0.075)
Burner operation pressure, pascals (psi) gauge	9.0×10^5 (130)	9.1×10^5 (132)	- NA[a]	6.3×10^5 (92)	6.6×10^5 (95)	6.9×10^5 (100)	6.8×10^5 (98)

Run No.	8	9	10	11
Temperature °C (°F)				
Primary chamber (Thermocouple No. ①)	690 (1280)	950 (1750)	590 (1100)	580 (1070)
Primary chamber (Thermocouple No. ②)	650 (1200)	930 (1700)	490 (910)	470 (880)
Primary chamber (Thermocouple No. ③)	730 (1350)	970 (1780)	620 (1150)	600 (1110)
Second chamber (Thermocouple No. ④)	600 (1120)	840 (1540)	520 (970)	550 (1020)
Second chamber (Thermocouple No. ⑤)	390 (730)	570 (1050)	300 (570)	350 (670)
Sample Point No. ② (Thermocouple No. ⑥)	160 (320)	290 (560)	190 (370)	240 (460)
Pressures				
Draft (Manometer No. △), pascals (in. H_2O) gauge	16 (0.065)	22 (0.090)	15 (0.060)	35 (0.140)
Burner operating pressure, pascals (psi) gauge	5.9×10^5 (85)	9.3×10^5 (135)	7.3×10^5 (105)	7.2×10^5 (105)

---

[a] Not determined.

The results of total pyrophosphate analysis for these 11 experiments were as follows:

Run No.	Pyrophosphates[a/] (gr/hr)
1	ND[b/]
2	ND
3	ND
4	ND
5	3.21
6	2.14
7	2.46
8	2.14
9	0.62
10	2.01
11	ND

[a/] Expressed as phosphorus.

[b/] Not detected.

In order to evaluate the effect of physical form on the efficiency with which malathion can be incinerated, five tests were made using an ~ 25% dust formulation. Results from these experiments are summarized in Tables 55 through 59. Two efficiencies of combustion have been calculated (see Table 56). The first considers only the quantity of actual malathion in the incinerator input and discharge. This efficiency calculation shows that > 99.99% of the malathion injected into the incinerator was at least partially degraded at all temperatures tested, 630 to 1040°C (1170 to 1900°F).

The second efficiency calculation includes not only the malathion that was left, but also all other organic phosphate species detected. Using this calculation, all five tests showed an efficiency of > 99.99% for the incinerator effluent gas.

Measurable quantities of total pyrophosphates were not detected in either the residues or the effluent gas from the incineration of 25% malathion dust. The colorimetric method being used for total pyrophosphate determination is based on the difference between ortho- and total phosphate content.

Table 55. SUMMARY OF 25% MALATHION WETTABLE POWDER EXPERIMENTS

Run No.	No. 2 fuel oil rate: Nominal burner size ℓ/hr (gal/hr)	No. 2 fuel oil rate: Actual rate ℓ/hr (gal/hr)	Pesticide feed rate: ~ 25% Malathion formulation kg/hr (lb/hr)	Pesticide feed rate: Contained malathion g/hr (lb/hr)[a]	Primary chamber temperature °C (°F)	Excess air[b] %	Retention time[c] sec: Primary chamber	Retention time[c] sec: Second chamber	Sampling time min	Off-gas flow rate[d] m^3/hr (1,000's of SCFH)
A	4.7 (1.25)	4.05 (1.07)	14.02 (30.9)	3,310 (7.33)	810 (1490)	43	4.2	4.5	60	201 (7.1)
B	9.5 (2.5)	8.52 (2.25)	19.23 (42.4)	4,580 (10.08)	1040 (1900)	37	3.8	3.9	60	184 (6.5)
C	4.7 (1.25)	4.09 (1.08)	13.15 (29.0)	3,130 (6.90)	730 (1340)	113	5.7	5.6	60	167 (5.9)
D	11.4 (3.0)	10.48 (2.77)	13.83 (30.5)	3,290 (7.25)	930 (1710)	156	1.9	1.8	60	408 (14.4)
E	3.8 (1.0)	3.63 (0.96)	6.30 (13.9)	1,100 (2.42)	630 (1170)	157	4.2	4.0	60	246 (8.7)

---

[a] Actual malathion content of the ~ 25% wettable powder formulation.

[b] Calculated according to Method 3 of "Standards of Performance for New Stationary Sources," Federal Register, 36(247):24876-24895, 23 December 1971.

[c] Retention time is defined as $\frac{V}{v}$, where v is the wet off-gas flow rate from the incinerator at the respective chamber temperature and pressure, and V is the volume of that chamber.

[d] As dry gas at one atmosphere pressure, and 21.1°C (70°F).

Table 56. RESIDUE AND OFF-GAS CHARACTERISTICS--25% MALATHION WETTABLE POWDER EXPERIMENTS

Run No.	Pesticide feed rate		Solid residue						Ratio of total residue to total formulation fed
	~ 25% Malathion formulation kg/hr (lb/hr)	Contained malathion[a] g/hr	Primary chamber			Second chamber			
			Total kg/hr (lb/hr)	Malathion conc. ppm	Total species[c] conc., ppm	Total kg/hr (lb/hr)	Malathion conc. ppm	Total species[c] conc., ppm	
A	14.02 (30.9)	3,310	2.68 (5.9)	5.6	5.6	1.22 (2.7)	1.2	1.2	0.28
B	19.23 (42.4)	4,580	2.04 (4.5)	0.6	1.3	0.73 (1.6)	1.9	1.9	0.14
C	13.15 (29.0)	3,130	2.77 (6.1)	0.4	0.4	0.63 (1.4)	2.4	2.4	0.26
D	13.83 (30.5)	3,290	2.04 (4.5)	< 0.3[b]	< 0.3	0.68 (1.5)	< 0.3[b]	< 0.3	0.20
E	6.30 (13.9)	1,100	1.18 (2.6)	1.5	1.5	0.68 (1.5)	1.1	1.1	0.29

Run No.	Malathion content of of off-gas g/hr	Malathion content of solid residues g/hr	Total malathion content of off-gas and solid residues g/hr	Total species[c] content of off-gas g/hr	Total species[c] content of solid residues g/hr	Total species[c] content of off-gas and solid residues g/hr	Ratio of malathion in off-gas to total malathion fed	Ration of total species[c] in off-gas to total malathion fed	Incineration efficiency[e] %	
									Malathion	Total species[c]
A	$< 1.5 \times 10^{-3}$[d]	1.7×10^{-2}	$< 1.8 \times 10^{-2}$	$< 1.5 \times 10^{-3}$	1.8×10^{-2}	$< 2.0 \times 10^{-2}$	$< 4.5 \times 10^{-7}$[d]	$< 4.5 \times 10^{-7}$	> 99.99	> 99.99
B	2.1×10^{-3}	2.7×10^{-3}	4.8×10^{-3}	2.1×10^{-3}	3.9×10^{-3}	6×10^{-3}	4.6×10^{-7}	4.6×10^{-7}	> 99.99	> 99.99
C	$< 1.5 \times 10^{-3}$[d]	2.6×10^{-3}	$< 4.1 \times 10^{-3}$	$< 3.7 \times 10^{-2}$	2.6×10^{-3}	$< 4.0 \times 10^{-2}$	$< 4.8 \times 10^{-7}$[d]	$< 1.2 \times 10^{-5}$	> 99.99	> 99.99
D	$< 1.4 \times 10^{-3}$[d]	$< 8 \times 10^{-4}$	$< 2.2 \times 10^{-3}$	$< 8 \times 10^{-3}$	$< 8 \times 10^{-4}$	$< 9 \times 10^{-3}$	$< 4.3 \times 10^{-7}$[d]	2.4×10^{-6}	> 99.99	> 99.99
E	$< 1.5 \times 10^{-3}$[d]	2.5×10^{-3}	$< 4.0 \times 10^{-3}$	$< 1.5 \times 10^{-3}$	2.5×10^{-3}	$< 4.0 \times 10^{-3}$	$< 1.4 \times 10^{-6}$[d]	$< 1.4 \times 10^{-6}$	> 99.99	> 99.99

---

a/ Actual malathion content of the ~ 25% wettable powder formulation.

b/ Malathion was not detected in this residue. The value shown represents the detection limit for malathion in this sample.

c/ Malathion as well as all other organic phosphate species detected.

d/ Malathion was not detected in this off-gas. The value shown represents the detection limit for malathion in the respective sample.

e/ Efficiency is defined as $\left[1 - \frac{\text{Quantity out}}{\text{Quantity in}}\right] \times 100$, where the Sample Points Nos. ② (the incinerator off-gas) and ③ (solid residues) and the quantity in is evaluated at Sample Point No. ① (the incinerator feed). Efficiencies have been calculated based on (a) malathion only and (b) the total organic phosphate species detected at at Sample Points Nos. ② and ③ .

Table 57. OFF-GAS COMPOSITION--25% MALATHION DUST INCINERATION[a]

					Total hydrocarbons analyzer			Orsat analyzer			
Run No.	Malathion mg/m^3	Total[c] species mg/m^3	SO_2 mg/m^3	NO_x[d] mg/m^3	Total hydrocarbons ppm	CO ppm	CH_4 ppm	O_2 vol. %	CO_2 vol. %	CO vol. %	Moisture vol. %
A	$< 7.0 \times 10^{-3}$[b]	$< 7.0 \times 10^{-3}$	17,650	36	0	0	2	6.6	10.9	0.2	7.1
B	1.0×10^{-2}	1.0×10^{-2}	6,890	17	< 1	< 1	2	6.0	10.8	0.2	7.9
C	$< 8.4 \times 10^{-3}$[b]	$< 2.1 \times 10^{-1}$	8,910	220	14	132	3	11.3	7.5	0.1	7.0
D	$< 3.2 \times 10^{-3}$[b]	$< 1.8 \times 10^{-2}$	2,880	1,550	3	10	< 1	12.9	6.1	0.0	7.8
E	$< 5.6 \times 10^{-3}$[b]	$< 5.6 \times 10^{-3}$	2,450	46	4	< 1	2	13.1	5.9	0.1	7.5

---

a/ As dry gas at one atmosphere pressure, and 21.1°C (70°F).

b/ Malathion was not detected in this off-gas. The value shown represents the detection limit for malathion in the respective sample.

c/ Malathion plus all other organic phosphate species detected.

d/ Calculated as NO_2.

Table 58. PARTICULATE SAMPLING SUMMARY--25% MALATHION WETTABLE POWDER EXPERIMENTS

Description	A	B	C	D	E
Vol. dry-gas - std. cond., nm^3	0.335	0.305	0.280	0.723	0.418
Percent moisture by vol.	7.1	7.9	7.0	7.8	7.5
Avg. stack temperature, °C	204.4	303.3	246.2	477.0	209.7
Stk. flow rate, dry, std. cond., nm^3/min	3.3	3.1	2.8	6.8	4.1
Actual stack flow rate, m^3/min	5.8	6.5	5.3	18.8	7.3
Percent isokinetic	95.9	94.3	96.3	101.5	97.7
Percent excess air	43	37	113	156	157
Particulates - partial catch					
Particulate wt. - partial, mg	11,200	10,100	5,520	10,800	5,500
Part. load - ptl, std. cn., mg/nm^3	33,500	33,000	19,700	14,900	13,100
Part. load - ptl., stk. cn, mg/m^3	19,300	15,600	10,400	5,390	7,390
Partic. emis. - partial, kg/hr	6.714	6.134	3.281	6.065	3.223
Particulates - total catch					
Particulate wt. - total, mg	11,300	10,100	6,160	10.800	5,550
Part. load - ttl., std. cn., mg/nm^3	33,600	33,100	22,000	14,900	13,200
Part. load - ttl., std. cn., corrected to 12% CO_2, mg/nm^3	37,000	36,800	35,100	29,300	26,900
Part. load - ttl., stk. cn., mg/m^3	19,400	15,700	11,600	5,400	7,460
Partic. emis. - total, kg/hr	6.733	6.152	3.664	6.081	3.253
Percent impinger catch	0.29	0.30	10.44	0.27	0.93

Table 59. OPERATIONAL DATA SUMMARY--25% MALATHION WETTABLE POWDER EXPERIMENTS

Run No.	A	B	C	D	E
Temperatures, °C (°F)					
Primary chamber (Thermocouple No. 1)	800 (1480)	1000 (1840)	670 (1230)	890 (1630)	610 (1130)
Primary chamber (Thermocouple No. 2)	810 (1490)	1040 (1900)	680 (1260)	840 (1540)	540 (1010)
Primary chamber (Thermocouple No. 3)	NA[a]	1040 (1900)	730 (1340)	930 (1710)	630 (1170)
Second chamber (Thermocouple No. 4)	650 (1210)	920 (1680)	600 (1120)	800 (1480)	550 (1030)
Second chamber (Thermocouple No. 5)	420 (790)	560 (1040)	410 (770)	600 (1120)	350 (670)
Sample Point No. ② (Thermocouple No. 6)	220 (430)	320 (600)	250 (490)	470 (870)	230 (450)
Pressures					
Draft (Manometer No. △), pascals (in. H_2O) gauge	15 (0.060)	27 (0.110)	16 (0.065)	62 (0.250)	29 (0.115)
Burner operation pressure pascals (psi) gauge	7.6×10^5 (110)	7.6×10^5 (110)	7.4×10^5 (107)	9.1×10^5 (132)	7.4×10^5 (108)
Pesticide injection air, pascals (psi) gauge	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	8×10^4 (12)	6×10^4 (9)

---

[a] Thermocouple burned out during the test.

In general, results of the ortho- and total phosphate analyses for a given sample were equal (within experimental error); and therefore indicated no measurable total pyrophosphate. However, a few samples showed a higher value for ortho- than for total phosphates. This inconsistency can be attributed to positive interference during the color formation step of the orthophosphate test. During subsequent nitric acid digestion for total phosphate analysis, it is very probable that the interfering substances were destroyed, thus giving a lower absorbance for the spectrophotometric measurement.

The results of the particulate sampling conducted on the malathion tests are shown in Table 58. Two modifications of the standard sampling method were made to facilitate the analysis of the sample for malathion content; benzene was used in the impingers rather than water, and a liquid nitrogen cold trap was added to the sample train in order to collect condensibles for malathion analysis. Acceptable isokinetic conditions were achieved in all runs. The loadings all exceed what can be considered low emission and indicate the need for a particulate control device when incinerating malathion dust formulations.

Upon completion of the experiments with malathion, the experimental apparatus was inspected for any deposits or residues of pesticide containing materials. Wall scrapings from the horizontal section of the incinerator stack, the first water scrubber, and the demister pad in the first water scrubber contained no detectable levels of malathion, or of any other organic phosphorus compound. Wall scrapings from the vertical section of the incinerator stack contained 0.5 ppm malathion. Thus, there was apparently no significant deposition of malathion or any other organic phosphorus compound in the experimental apparatus.

DISCUSSION

Minor operating problems were encountered during the 57% malathion EC tests. Plugging of the demister in the first stage water scrubber (Manometer No. △4, Figure 5, p. 27) was observed, primarily during tests conducted at low draft (see Table 54). In addition, a visible white plume was noted emitting from the scrubber system exhaust. These same problems, i.e., inability to remove P_2O_5 from the effluent gas stream and plugging of filter elements had also been encountered during recent studies of the incineration of the organophosphorus chemical warfare agents GB and VX (Wynne[11] and Capasso et al.[12]).

References

1. Cyanamid International, Malathion Insecticide for Adult Mosquito Control (Bulletin), Wayne, New Jersey (undated).

2. Metcalf, R. L., and R. B. March, "The Isomerization of Organic Thiophosphate Insecticides," J. Econ. Entomol., 46:288-294 (April 1953).

3. McPherson, J. B., Jr., and G. A. Johnson, "Thermal Decomposition of Some Phosphorothioate Insecticides," J. Agr. Food Chem., 4(1):42-49 (January 1956).

4. Smith, W. M., Jr., and J. O. Ledbetter, "Hazards from Fires Involving Organophosphorus Insecticides," Amer. Ind. Hyg. Assoc. J., 32(7): 468-474 (July 1971).

5. Kennedy, M. V., B. J. Stojanovic, and F. L. Shuman, Jr., "Chemical and Thermal Methods for Disposal of Pesticides," Res. Rev., 29:89-104 (1969).

6. Melnikov, N. N., Chemistry of Pesticides, Springer-Verlag, New York, pp. 357-359 (1971).

7. Stojanovic, B. J., F. Hutto, M. V. Kennedy, and F. L. Shuman, Jr., "Mild Thermal Degradation of Pesticides," J. Environ. Quality, 1(4):397-401 (1972).

8. Putnam, R. C., F. Ellison, R. Protzmann, and J. Hilovsky, "Organic Pesticides and Pesticide Containers--A Study of their Decontamination and Combustion," EPA-SW-21C-71 (PB 202 202) (1971).

9. EPA Compendium of Registered Pesticides, Vol. III, U.S. Environmental Protection Agency (1973).

10. Midwest Research Institute, "Initial Scientific and Minieconomic Review of Malathion" (Draft), EPA Contract No. 68-01-2448 (September 1974).

11. Wynne, D. J., "Pilot-Scale Incineration of GB and VX and the Containment of Gaseous Products," Edgewood Arsenal Technical Report No. EATR 4734, U.S. Army Munitions Command, Edgewood Arsenal, Maryland (May 1973).

12. Capasso, N. S., L. Buckles, P. Cavey, F. Hildebrandt, and I. I. Stevens, U.S. Army Munitions Command, Edgewood Arsenal, Maryland; personal communication to Mr. Thomas L. Ferguson and Mr. Fred J. Bergman (14 September 1973).

V. TOXAPHENE

PESTICIDE DESCRIPTION

Physical Properties

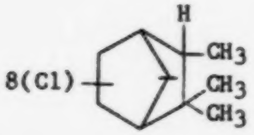
Chemical Name: Chlorinated camphene, octachlorocamphene

Common Name: Toxaphene

Trade Names: Agricide® Maggott Killer, Alltox®, Chem-Phene®, Estonox®, Phenacide®, ChlorChem T-590, Motox, Phenatox®, Strobane-T®, Toxakil®

Pesticide Class: Insecticide, chlorinated hydrocarbon

Structural Formula:



(Mixed isomers of chlorinated camphene (67-69% chlorine, at least 175 polychlorinated 10-carbon compounds have been detected[1]/)

Empirical Formula: $C_{10}H_{10}Cl_8$

Molecular Weight: 414

Physical State: Waxy solid

Melting Point: 70 to 95°C; softening point 70°C minimum

Boiling Point: Decomposes

Vapor Pressure: 0.17 to 0.40 mm Hg at 25°C
3.0 to 4.0 mm Hg at 90°C

Specific Gravity: 1.65 at 25°C

Density:

Temperature (°C)	Pounds/Gallon
100	13.6
90	13.7
80	13.8

Viscosity:	Temperature (°C)	Saybolt-Universal (sec)	Poises
	100	400	1.4
	110	260	0.9
	120	174	0.6
	130	120	0.4

Solubility:	Solvent	Grams/100 ml at 27°C
	Acetone	all proportions
	Benzene	all proportions
	Carbon tetrachloride	all proportions
	Ethylene dichloride	all proportions
	Toluene	all proportions
	Xylene	all proportions
	Hexane	all proportions
	Turpentine	below 350
	Kerosene	above 280
	Fuel oil	below 250
	Isopropyl alcohol	below 15
	95% Ethyl alcohol	below 10
	Water at 25°C	0.4 ppm

Chemical Properties

Toxaphene is reported to dehydrochlorinate in the presence of alkali upon prolonged exposure to sunlight and at temperatures of about 155°C.[2] Reduction with sodium in isopropyl alcohol is the analytical method for total chloride.

Production and Use

Toxaphene is a broad-spectrum insecticide (contact and stomach poison) which is used on a large number of agricultural crops, livestock, and ornamentals.

It has been estimated that the 1972 domestic production of toxaphene was 70 to 95 million pounds (von Rümker et al.).[3]

The toxaphene is formulated as 10 and 15% granular, 20% dust, and 6 and 8 lb/gal emulsifiable concentrates. Other formulations are low-volume concentrates, wettable powders, solutions, and combination formulations with other insecticides. These formulations are available under different brand names and in varying concentrations of active ingredient.

FORMULATIONS TESTED

The two toxaphene formulations tested were a 60% EC and a 20% dust.

60% EC

Name: Arcadian® Toxaphene EM-6

Manufacturer: Allied Chemical Corporation, Morristown, New Jersey

Composition: Active Ingredients

Toxaphene (technical chlorinated camphene, 67 to 69% chlorine)	60.00%
Petroleum Distillate (minimum unsulfonated residue 97%)	30.34%
Xylene	6.66%
Inert Ingredients	3.00%
Total	100.00%

Registration: EPA Reg. No. 218-643

Lot No.: SO-108022

20% Dust

Name: Cotton States Toxaphene 20% Dust

Manufacturer: Cotton States Chemical Co., Inc., Monroe, Louisiana

Composition: Active Ingredients

Toxaphene*	20.00%
Inert Ingredients	80.00%
Total	100.00%

---

* Technical chlorinated camphene (chlorine content 67 to 69%)

Registration: EPA Reg. No. 1339-6

Pesticide Size Specifications: Formulated in attapulgite clay such that at least 90% passes through a 44 μ (325 mesh) sieve

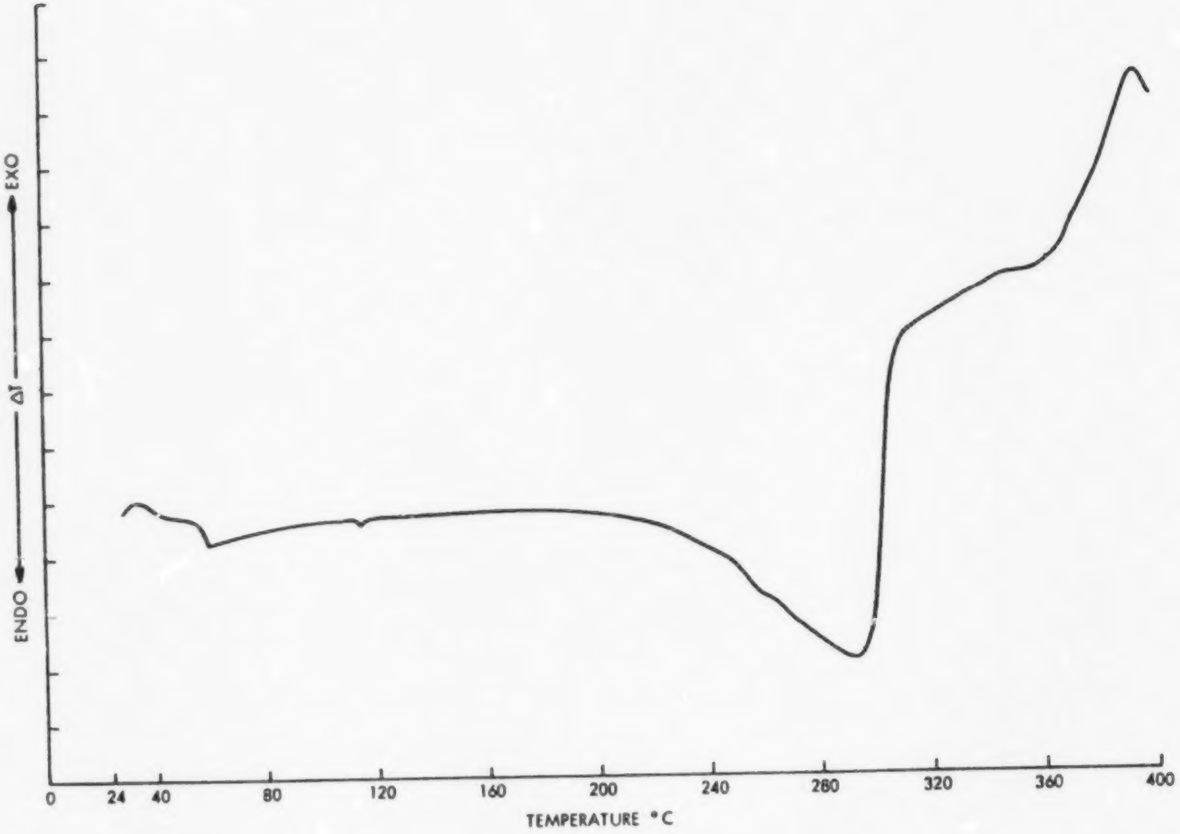
PRELIMINARY THERMAL ANALYSIS

Laboratory thermal analyses of toxaphene gave the following results:

Sample	Test	Test Method	Result
Toxaphene 20% dust	Sulfur	ASTM D-129	3.27%
	Calorific value	ASTM D-240	3.286×10^6 J/kg (1,414 Btu/lb)
Toxaphene 60% liquid form	Sulfur	ASTM D-129	2.35%
	Calorific value	ASTM D-240	2.577×10^7 J/kg (11,089 Btu/lb)

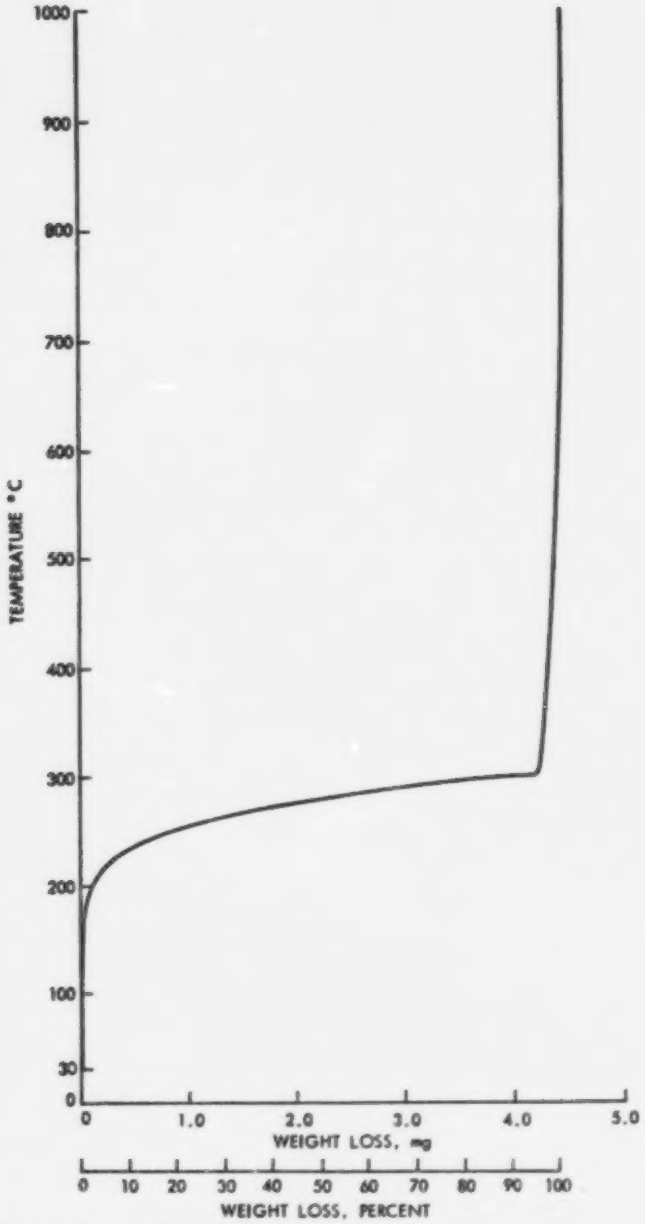
Figures 37 and 38 show the results of DTA and TGA of the technical grade toxaphene. DTA data show no prominent endotherm or exotherm at lower temperatures. However, as the temperature reaches about 290°C, sharp decomposition is observed and continues to 400°C (instrument limit). This decomposition process is substantiated by the TGA data which indicate almost 95% of the initial weight is lost when temperature reaches 300°C.

Figures 39 and 40 show the results of DTA and TGA of the 20% toxaphene dust formulation. The DTA data show no significant exotherms or endotherms; however, a slow decomposition process is observed. This decomposition process is substantiated by the TGA which indicates slow weight loss all the way to about 700°C. The weight loss takes place mainly at two temperature ranges, one quite abruptly at about 190 to 260°C (about 20% weight loss), and the other, rather gradually, from 260 to 710°C (about 15% weight loss). At 710°C about 35% of the original weight is gone, compared to the nominal 20% toxaphene content of the formulation. No further weight loss is observed from 710 to 1000°C.



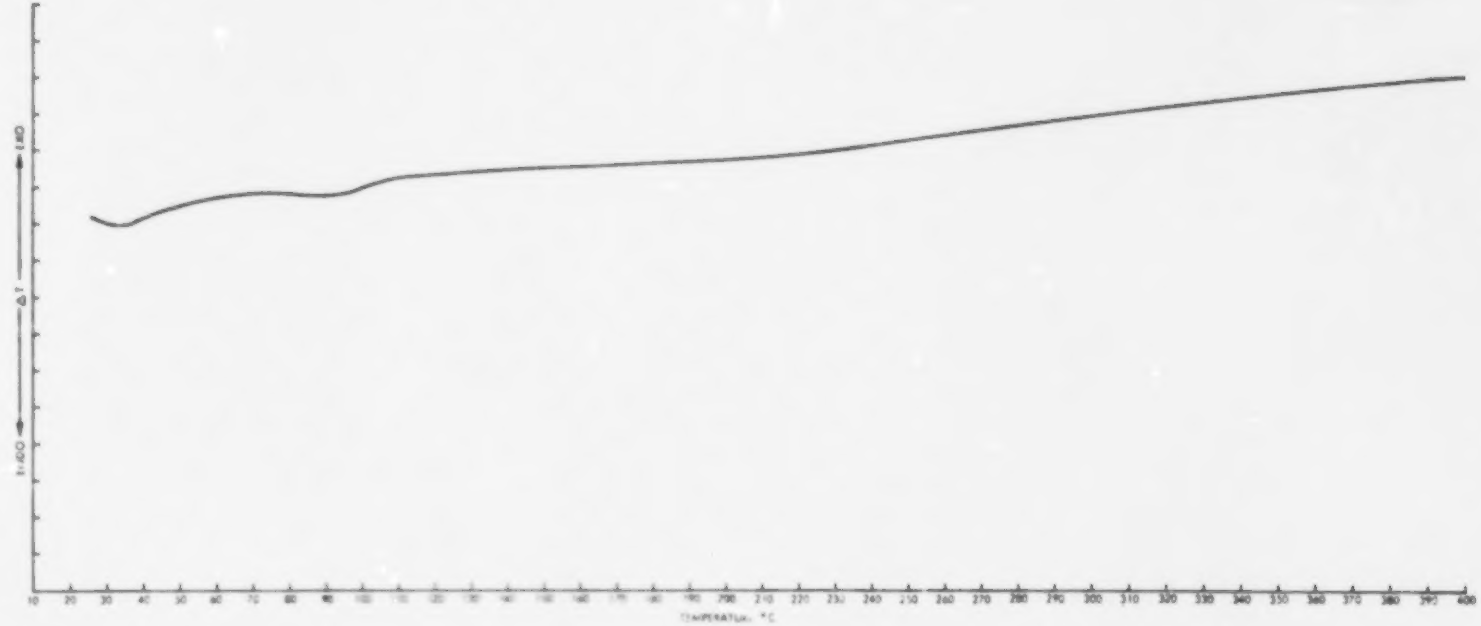
Reference: Empty pan
Prog. mode: Heat
Rate: 10°C/min
Start: 24°C

Figure 37. DTA of technical toxaphene



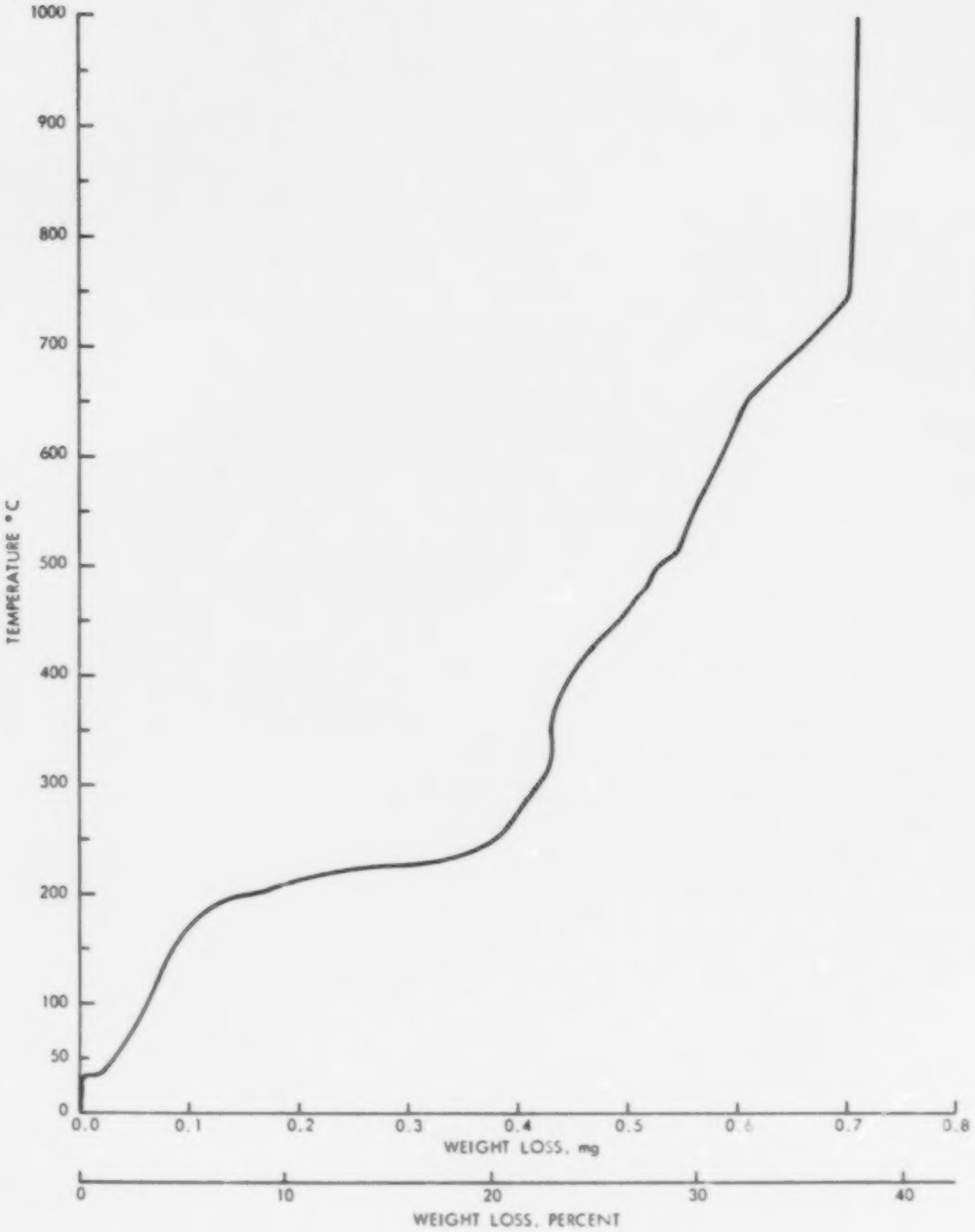
Sample weight: 4.404 mg
Heating rate: 20°C/min
Environment: ~ 20 ml/min air (20% O_2, 80% N_2)

Figure 38. TGA of technical toxaphene



Reference: Empty pan
Prog. mode: Heat
Rate: 10°C/min
Start: 26°C

Figure 39. DTA of ~ 20% toxaphene dust



Sample weight: 1.878 mg
Heating rate: 20°C/min
Environment: ~ 20 ml/min air (20% O_2, 80% N_2)

Figure 40. TGA of ~ 20% toxaphene dust

Figures 41 and 42 show the results of DTA and TGA of a sample of recrystallized toxaphene obtained by evaporation of a sample of the liquid formulation. The DTA data (Figure 41) show an endotherm at about 306°C, which may be only a phase change, as TGA data in Figure 42 show no significant weight loss at this temperature. However, prior to this endotherm, decomposition is observed which is substantiated by the abrupt weight loss from 180 to 280°C in the TGA. About 95% of the original weight is gone at 280°C. Essentially no more than 3% additional weight loss is observed from 280 to 1000°

METHODS OF ANALYSIS

Apparatus

A Micro-Tek 2000R gas chromatograph equipped with a 3-ft, 4 mm I.D. glass column (packed with 1.5% OV-17 + 1.95% QF-1 on 80/100 mesh Supelcoport from Supelco, Inc., Bellefonte, Pennsylvania) and a tritium electron capture detector, maintained at a voltage of 20 V DC, was used for gas chromatographic analysis. The chromatographic operating conditions were: injector temperature, 210°C; column temperature, 195°C; detector temperature, 180°C; carrier flow rate, 80 ml/min, N_2; and a purge gas flow rate, 120 ml/min, N_2.

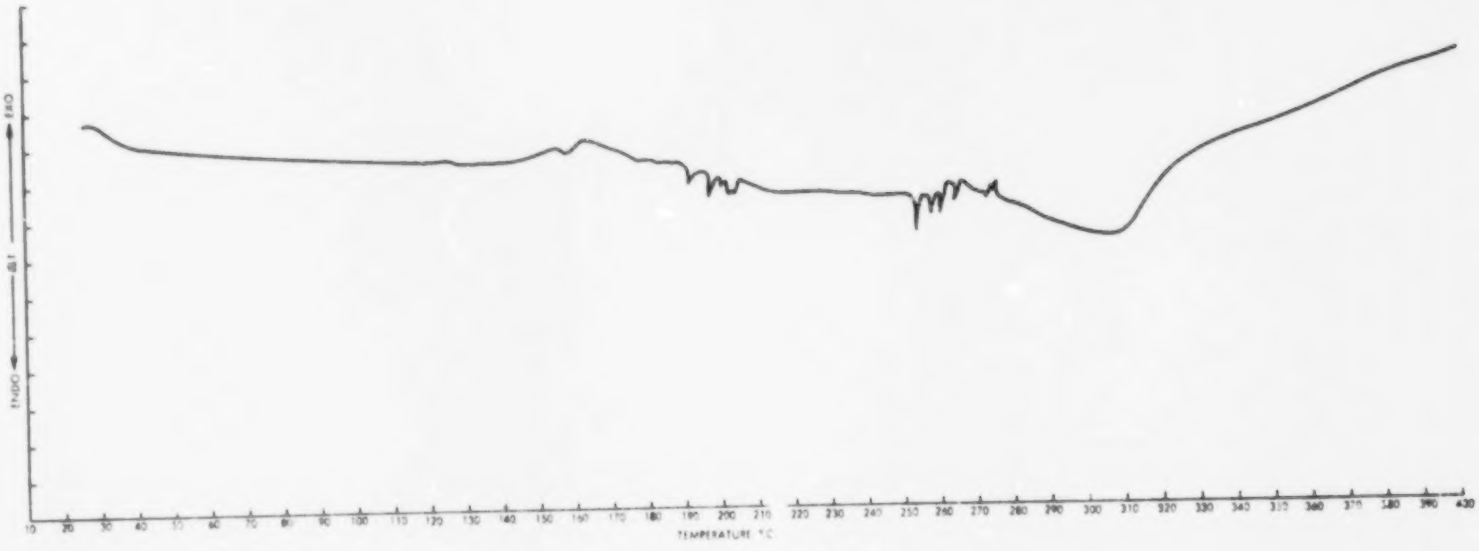
A Hewlett-Packard 3380A Integrator was used for peak quantification.

Reagents and Materials

Analytical reagents toxaphene (68.9% Cl^-) and aldrin (97% pure), were used for preparing standards. Solvents used were pesticide grade 2,2,4-trimethylpentane (Mallinckrodt) for standard preparation and all impingers, and pesticide grade hexane (Matheson, Coleman, and Bell) for extraction of hexylene glycol traps from the second stage scrubber. All laboratory glassware (beakers, vials, etc.) was washed in Alconox detergent (Scientific Products) and rinsed with deionized distilled water and reagent grade acetone (Fisher Scientific).

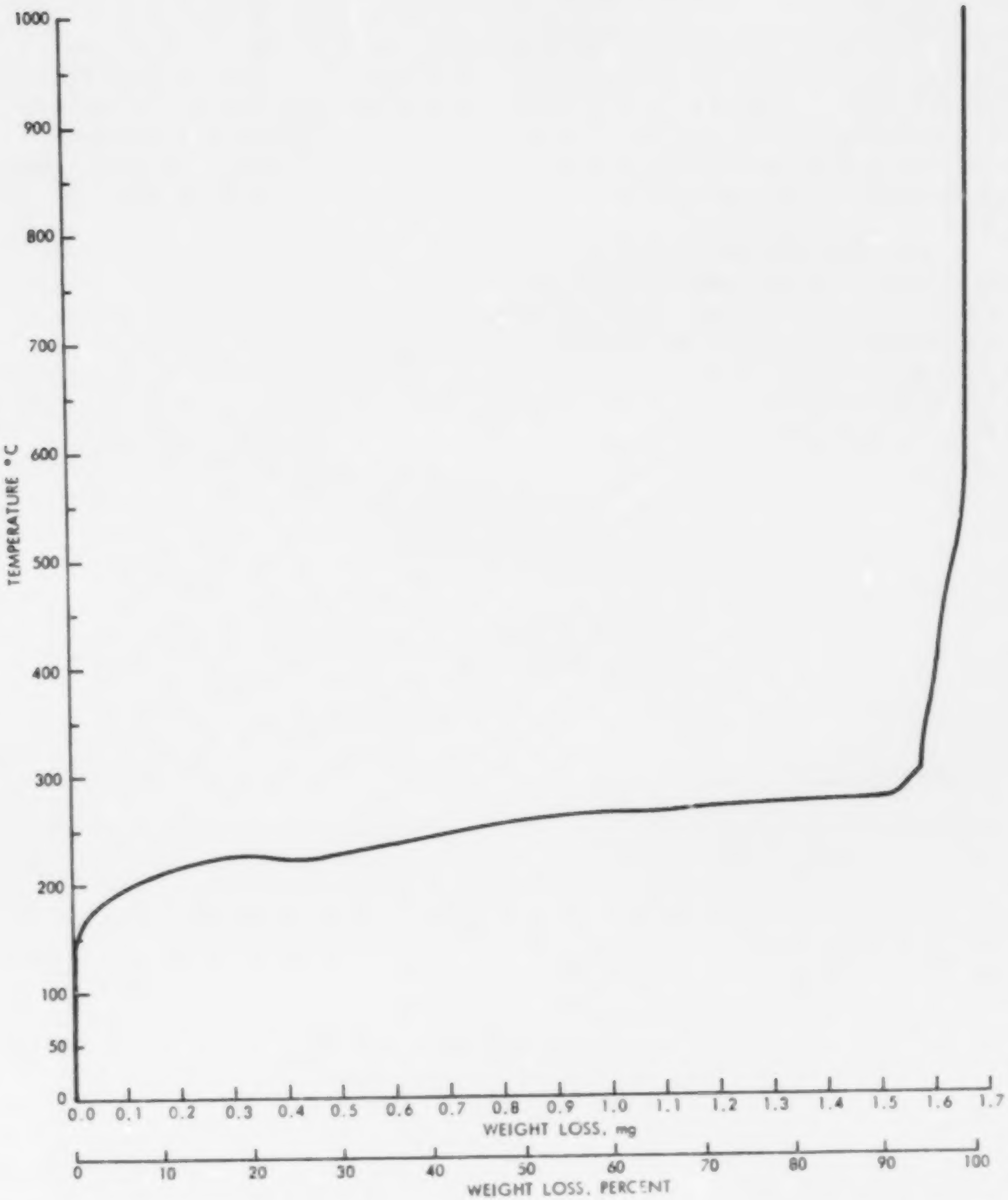
Standards and Calibration Curves

The solid standard, aldrin, provided by USEPA, was used to prepare a stock solution of 100 μg/ml and appropriate dilutions were made to obtain linear results (linear range used: 0 to 200 pg). A toxaphene standard was made up in the same manner and used for a standard curve for the incinerator feed samples.



Reference: Glass beads
Prog. mode: Heat
Rate: 10°C/min
Start: 26°C

Figure 41. DTA of recrystallized toxaphene



Sample weight: 1.674 mg
Heating rate: 20°C/min
Environment: ~ 20 ml/min air (20% O_2, 80% N_2)

Figure 42. TGA of recrystallized toxaphene

Procedure for Sample Preparation

All impingers, washes, and blank solutions, except the hexylene glycol samples from the second stage scrubber, were taken just to dryness in their original French Square, sample bottles. Ten milliliters of the hexylene glycol samples were extracted with n-hexane and the extract was taken just to dryness. All samples were taken up again in appropriate amounts of 2,2,4trimethylpentane just prior to gas chromatography.

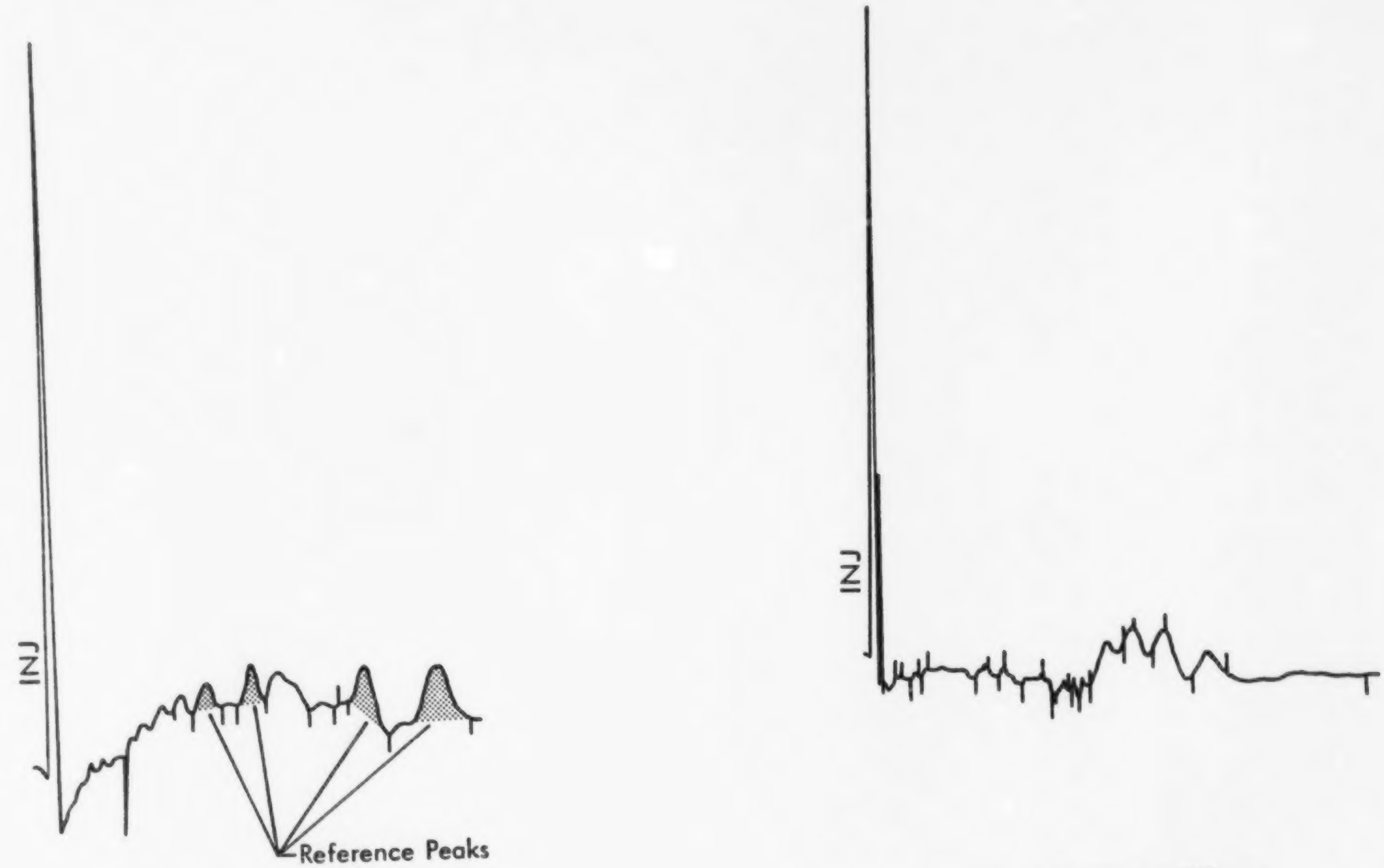
The mass of collected particulates was determined for all samples collected from incineration of toxaphene dust as follows: samples were taken to dryness under a hood in clean, dessicated, tared 250-ml beakers and dessicated 2 days before final weighing. The residue was extracted with 2,2,4-trimethylpentane (two 10 to 15 ml portions) and the extract was taken just to dryness. The silica gel was extracted with sufficient 2,2,4-trimethylpentane to cover the silica gel and a 20 ml portion pipetted out and taken to dryness. Twenty milliliter portions of the blank impinger solutions (2,2,4-trimethylpentane and acetone) were pipetted out into vials and taken to dryness. All samples were then taken up again in appropriate amounts of 2,2,4-trimethylpentane just prior to gas chromatography.

Portions of all cleanout samples (primary chamber, secondary chamber, etc.) were weighed out and extracted and the extracts were analyzed for toxaphene (chlorinated hydrocarbons).

Analysis and Discussion

The complexity of the toxaphene chromatogram has been illustrated in the literature, including at least 175 polychlorinated 10-carbon compounds.[1] (Representative chromatograms for both the liquid toxaphene formulation and the incinerator effluent are given in Figure 43). For this reason, it is virtually impossible to pick out toxaphene as such from the samples collected after each incineration. Therefore, it was decided to quantitate all the chromatographic peaks based on an aldrin standard curve. However, incinerator feed samples were quantitated relative to the actual toxaphene response. This was accomplished by using four of the most prominent and reproducible peaks in the toxaphene mixture.

The sensitivity of the instrument for aldrin is 1 pg. The sensitivity for the toxaphene standard, based on the four most prominent peaks, is 0.5 ng. Since the feed samples consist of 60% toxaphene, appropriate dilutions were necessary to bring its concentration to the calibration range.



a - 60% Toxaphene Formulation

b - Incinerator Effluent
(Sample Point No. ② ,
Figure 5, p. 27)

Figure 43. Representative toxaphene chromatograms

(External calibration method: Hewlett-Packard Integrator Model 3380A instruction manual, pp. 3-18.)

During the course of the toxaphene analysis, frequent ghosting was observed in the chromatogram, which necessitated rerunning of several samples where ghosts interfered. The detector required cleaning twice, and consequently there was considerable down time on the instrument used for toxaphene analysis.

TEST CONDITIONS AND RESULTS

Eleven tests were made using the 60% EC toxaphene formulation. The temperature of the primary chamber was varied between the lower operating limit of the incinerator, ~ 650°C (1200°F), and 1000°C (1830°F).

The results of these 11 tests are shown in Tables Nos. 60 through 62. As has been discussed above, technical grade toxaphene consists of a number of chlorinated hydrocarbons, including at least 175 polychlorinated 10-carbon compounds.[1] For this reason, the efficiency of toxaphene incineration was evaluated based on actual toxaphene content of the incinerator feed (Sample Point No. ①) versus the total chlorinated hydrocarbons detected in the incinerator effluent (Sample Point No. ②). No solid residues were formed during the incineration of liquid toxaphene, and therefore, do not enter into the efficiency calculation. The percent efficiency calculations show that > 99.99% of the toxaphene injected into the incinerator was degraded for all 11 experiments, i.e., over the ranges of excess air, operating temperature, and incinerator feed rate investigated.

There is no correlation between operating temperature and the relative amount of unburned "toxaphene" discharged (as shown by the "Ratio of Chlorinated Hydrocarbon Content of the Off-Gas to Toxaphene Fed" column of Table 60. Significantly higher levels were discharged, however, from Tests 5 and 7. These two tests also had the shortest retention times in the primary chamber (2.4 and 2.2 sec, respectively).

Six tests were made using an ~ 20% dust formulation of toxaphene in order to evaluate the effect of physical form on incineration efficiency. The results of the six tests are summarized in Tables 63 through 67. Nominal conditions were the high feed rate (7.5 lb active ingredient/hr), "high" and "low temperature" 1000°C (1830°F) and 650°C (1200°F), respectively, tively, and "high" and "low" excess air (150 and 50%, respectively).

Table 60. SUMMARY OF 60% TOXAPHENE EC EXPERIMENTS

	Incinerator feed								
Run No.	Nominal burner size ℓ/hr (gal/hr)	Total feed rate ℓ/hr (gal/hr)	Toxaphene rate g/hr (lb/hr)[a]	Toxaphene rate ℓ/hr (gal/hr)[b]	Toxaphene concentration mg/ml	No. 2 fuel oil rate ℓ/hr (gal/hr)	Primary chamber temperature °C (°F)	Flame temperature[c] °C (°F)	Excess[d] air %
1	3.8 (1.0)	3.41 (0.90)	1,250 (2.75)	2.38 (0.63)	370	1.02 (0.27)	620 (1150)	-	349
2	3.8 (1.0)	3.71 (0.98)	1,220 (2.70)	2.31 (0.61)	330	1.40 (0.37)	630 (1160)	-	198
3	4.7 (1.25)	4.16 (1.10)	1,540 (3.40)	2.91 (0.77)	375	1.25 (0.33)	680 (1260)	-	160
4	11.3 (3.0)	9.16 (2.42)	1,520 (3.35)	2.84 (0.75)	165	6.32 (1.67)	1040 (1900)	1040 (1910)	47
5	11.3 (3.0)	9.16 (2.42)	1,250 (2.75)	2.35 (0.62)	135	6.81 (1.80)	960 (1800)	-	124
6	11.3 (3.0)	8.74 (2.31)	3,240 (7.15)	6.09 (1.61)	370	2.65 (0.70)	1040 (1900)	1140 (2090)	71
7	11.3 (3.0)	10.14 (2.68)	2,340 (5.15)	4.43 (1.17)	230	5.71 (1.51)	990 (1820)	1160 (2120)	128
8	4.7 (1.25)	4.20 (1.11)	2,220 (4.90)	4.20 (1.11)	530	- 0 -	670 (1240)	-	212
9	3.8 (1.0)	2.84 (0.75)	1,090 (2.40)	2.08 (0.55)	385	0.76 (0.20)	660 (1220)	-	154
10	4.7 (1.25)	4.01 (1.06)	2,110 (2.65)	4.01 (1.06)	525	- 0 -	680 (1260)	1140 (2080)	228
11	3.8 (1.0)	3.67 (0.97)	1,070 (2.35)	2.01 (0.53)	290	1.66 (0.44)	650 (1200)	-	150

	Retention time[e] sec						
Run No.	Primary chamber	Second chamber	Sampling time min	Off-gas flow rate[f] m^3/hr (1,000's of SCFH)	Chlorinated hydrocarbon content of off-gas g/hr	Ratio of chlorinated hydrocarbon content of the off-gas to toxaphene fed	Efficiency[g] %
1	5.3	4.9	30	156 (5.5)	4×10^{-3}	3×10^{-6}	> 99.99
2	5.0	4.6	30	159 (5.6)	2×10^{-3}	2×10^{-6}	> 99.99
3	4.6	4.4	30	156 (5.5)	1×10^{-3}	9×10^{-7}	> 99.99
4	3.4	3.5	30	156 (5.5)	4×10^{-4}	3×10^{-7}	> 99.99
5	2.4	2.4	30	232 (8.2)	4.1×10^{-2}	3.3×10^{-5}	> 99.99
6	3.8	3.9	30	136 (4.8)	8×10^{-5}	2×10^{-8}	> 99.99
7	2.2	2.2	30	249 (8.8)	4.0×10^{-2}	1.7×10^{-5}	> 99.99
8	5.2	5.1	30	144 (5.1)	9×10^{-3}	4×10^{-6}	> 99.99
9	6.6	6.2	30	116 (4.1)	1×10^{-5}	9×10^{-9}	> 99.99
10	6.5	6.4	30	113 (4.0)	5×10^{-3}	2×10^{-6}	> 99.99
11	6.7	6.5	30	110 (3.9)	1×10^{-5}	1×10^{-8}	> 99.99

---

[a] Actual toxaphene content of the incinerator feed.

[b] Volume per hour of the liquid toxaphene formulation.

[c] The flame temperature was observed at a point approximately 15 cm (6 in.) in from the fron wall of the incinerator.

[d] Calculated according to Method 3 of "Standards of Performance for New Stationary Sources," Federal Register, 36(247):24876-24895 (23 December 1971).

[e] Retention time is defined as $\frac{V}{v}$, where v is the wet off-gas flow rate from the incinerator at the respective chamber temperature and pressure, and V is the volume of that chamber.

[f] As dry gas at one atmosphere pressure, and 21.1°C (70°F).

[g] Efficiency is defined as: $\left[1 - \frac{\text{quantity out}}{\text{quantity in}}\right] \times 100$, where quantity out is the amount of chlorinated hydrocarbons detected at Sample Point No. ② (incinerator off-gas), and amount in is the amount of toxaphene detected at Sample Point No. ① (incinerator feed).

Table 61. OFF-GAS COMPOSITION--60% TOXAPHENE EC INCINERATION[a/]

				Total hydrocarbons analyzer			Orsat analyzer			
Run No.	Chlorinated hydrocarbons[b/] mg/m^3	SO_2 mg/m^3	NO_x[d/] mg/m^3	Total hydrocarbons ppm	CO ppm	CH_4 ppm	O_2 vol. %	CO_2 vol. %	CO vol. %	Moisture vol. %
1	2.6×10^{-2}	ND[c/]	439	13	> 201[e/]	3	16.4	4.1	0.4	3.9
2	1.3×10^{-2}	672	257	7	194	1	14.5	4.5	0.3	6.6
3	9.0×10^{-3}	30	392	6	17	3	13.3	5.5	0.0	7.4
4	2.8×10^{-3}	240	ND[c/]	222	3,440	35	7.1	10.0	0.3	11.9
5	1.8×10^{-1}	72	ND	11	2	< 1	11.9	6.8	0.0	5.9
6	5.7×10^{-4}	205	133	9	ND	1	9.0	8.9	0.0	10.4
7	1.6×10^{-1}	122	2,490	ND	34	3	12.0	6.5	0.0	7.3
8	6.0×10^{-2}	85	ND	< 1	12	5	14.5	4.8	0.1	7.6
9	8.6×10^{-5}	114	11	124	4,000	5	13.0	6.1	0.0	6.8
10	4.1×10^{-2}	59	322	435	2,220	62	14.9	4.4	0.1	8.5
11	1.0×10^{-4}	110	ND	53	107	3	12.9	6.0	0.0	9.8

---

a/ As dry gas at one atmosphere pressure, and 21.1°C (70°F).
b/ Total chlorinated hydrocarbon species detected.
c/ Not detected.
d/ Calculated as NO_2.
e/ Analyzer attenuation setting too low.

Table 62. OPERATIONAL DATA SUMMARY--60% TOXAPHENE EC EXPERIMENTS

Run No.	1	2	3	4	5	6
Temperature °C (°F)						
Primary chamber (Thermocouple No. ①)	580 (1080)	590 (1100)	650 (1200)	1010 (1850)	940 (1730)	1010 (1850)
Primary chamber (Thermocouple No. ②)	530 (980)	540 (1000)	590 (1100)	980 (1800)	900 (1660)	990 (1810)
Primary chamber (Thermocouple No. ③)	620 (1150)	630 (1160)	680 (1260)	1040 (1900)	980 (1800)	1040 (1900)
Second chamber (Thermocouple No. ④)	570 (1050)	570 (1060)	620 (1140)	890 (1640)	860 (1580)	870 (1590)
Second chamber (Thermocouple No. ⑤)	370 (690)	390 (740)	420 (780)	550 (1020)	590 (1100)	600 (1110)
Sample Point No. ② (Thermocouple No. ⑥)	220 (430)	200 (400)	200 (400)	260 (500)	380 (710)	330 (620)
Pressures						
Draft (Manometer No. △1), pascals (in H_2O) gauge	21 (0.085)	19 (0.075)	19 (0.075)	20 (0.080)	37 (0.150)	21 (0.085)
Burner operation pressure, pascals (psi) gauge	7.6 x 10^5 (110)	7.6 x 10^5 (110)	7.6 x 10^5 (110)	9.3 x 10^5 (135)	9.3 x 10^5 (135)	9.3 x 10^5 (135)
Scrubber liquids[a]						
1st Stage, H_2O scrubber						
Volume, ℓ (gal.)	1200 (318)	1120 (295)	1190 (315)	1160 (306)	1170 (309)	1140 (302)
Total species conc.,[b] mg/ℓ	5 x 10^{-4}	6 x 10^{-4}	1 x 10^{-3}	7 x 10^{-4}	6 x 10^{-4}	4 x 10^{-3}
2nd Stage, hexalene glycol scrubber						
Volume, ℓ (gal.)	109 (28.8)	109 (28.8)	109 (28.8)	110 (29.1)	111 (29.3)	111 (29.3)
Total species conc. change,[b] mg/ℓ	9 x 10^{-2}	5 x 10^{-3}	6 x 10^{-2}	ND[d]	ND	2 x 10^{-1}
3rd Stage, H_2O scrubber						
Volume, ℓ (gal.)	1880 (497)	1750 (463)	1750 (463)	1750 (463)	1750 (463)	1730 (457)
Total species conc.,[b] mg/ℓ	2 x 10^{-4}	4 x 10^{-4}	2 x 10^{-3}	1 x 10^{-3}	8 x 10^{-5}	2 x 10^{-4}
Scrubber system						
Effluent gas (Sample Point No. ⑨)[c]						
Total species conc., mg/m^3	1 x 10^{-1}	7 x 10^{-2}	6 x 10^{-2}	< 1 x 10^{-2}	1	3 x 10^{-2}

Table 62. (Concluded)

Run No.	7	8	9	10	11
Temperature °C (°F)					
Primary chamber (Thermocouple No. ①)	990 (1820)	650 (1200)	640 (1190)	660 (1220)	640 (1180)
Primary chamber (Thermocouple No. ②)	960 (1760)	600 (1120)	550 (1030)	620 (1140)	540 (1000)
Primary chamber (Thermocouple No. ③)	1000 (1830)	680 (1250)	660 (1220)	680 (1260)	650 (1210)
Second chamber (Thermocouple No. ④)	860 (1580)	580 (1030)	590 (1100)	590 (1090)	580 (1070)
Second chamber (Thermocouple No. ⑤)	600 (1120)	370 (700)	400 (750)	390 (730)	370 (700)
Sample Point No. ② (Thermocouple No. ⑥)	390 (730)	220 (420)	190 (370)	190 (370)	190 (370)
Pressures					
Draft (Manometer No. △1), pascals (in H_2O) gauge	41 (0.165)	24 (0.095)	15 (0.060)	16 (0.065)	16 (0.065)
Burner operation pressure, pascals (psi) gauge	9.3×10^5 (135)	7.4×10^5 (108)	7.9×10^5 (115)	8.1×10^5 (117)	8.1×10^5 (118)
Scrubber liquids[a]					
1st Stage, H_2O scrubber					
Volume, ℓ (gal.)	1160 (306)	1140 (302)	1230 (324)	1200 (318)	1180 (311)
Total species conc.,[b] mg/ℓ	4×10^{-2}	3×10^{-3}	2×10^{-3}	1×10^{-3}	2×10^{-4}
2nd Stage, hexalene glycol scrubber					
Volume, ℓ (gal.)	110 (29.1)	109 (28.9)	108 (28.6)	106 (28.1)	104 (27.6)
Total species conc. change,[b] mg/ℓ	2×10^{-1}	NA	ND	7×10^{-2}	ND
3rd Stage, H_2O scrubber					
Volume, ℓ (gal.)	1790 (474)	1750 (463)	1950 (514)	1900 (503)	1820 (480)
Total species conc.,[b] mg/ℓ	NA[e]	2×10^{-4}	4×10^{-3}	3×10^{-3}	2×10^{-3}
Scrubber system					
Effluent gas (Sample Point No. ⑨)[c] Total species conc., mg/m³	$< 1 \times 10^{-2}$	$< 1 \times 10^{-2}$	$< 2 \times 10^{-2}$	5×10^{-1}	$< 1 \times 10^{-2}$

---

[a] Scrubber water (Scrubbers 1 and 3) was used once through, while the hexylene glycol (Scrubber 2) was recycled. The concentrations reported for hexylene glycol, therefore, are the concentration changes (increases) detected during the respective tests.

[b] Total chlorinated hydrocarbon species detected.

[c] As the wet gas at 1 atm pressure and 21.70°C (70°F). Chlorinated hydrocarbons were not detected in all major elements of the sample train (i.e., impingers); the values given include the detection limits for chlorinated hydrocarbons in these elements.

[d] No increase in concentration detected.

[e] No analysis.

Table 63. SUMMARY OF 20% TOXAPHENE DUST EXPERIMENTS

	No. 2 fuel oil rate		Pesticide feed rate					Retention time sec[d]			
Run No.	Nominal burner size ℓ/hr (gal/hr)	Actual rate ℓ/hr (gal/hr)	~ 20% Toxaphene formulation kg/hr (lb/hr)	Contained toxaphene[a] g/hr (lb/hr)	Primary chamber temperature °C (°F)	Flame temperature[b] °C (°F)	Excess air[c] %	Primary chamber	Second chamber	Sampling time min	Off-gas flow rate[e] m^3/hr (1,000's of SCFH)
A	3.8 (1.0)	3.86 (1.02)	14.92 (32.9)	3,520 (7.76)	670 (1240)	900 (1650)	94	7.7	8.3	60	195 (6.9)
B	4.7 (1.25)	4.05 (1.07)	16.47 (36.3)	2.750 (6.06)	670 (1240)	970 (1770)	166	5.3	5.7	60	283 (10.0)
C	9.5 (2.5)	8.71 (2.30)	18.42 (40.6)	3,060 (6.75)	1010 (1850)	-- --	53	2.9	3.2	30	337 (11.9)
D	9.5 (2.5)	8.78 (2.32)	18.51 (40.8)	3,850 (8.49)	1030 (1880)	920 (1690)	44	3.4	4.1	60	278 (9.8)
E	11.4 (3.0)	9.69 (2.56)	16.51 (36.4)	3,430 (7.56)	970 (1770)	1050 (1920)	122	2.5	2.8	60	416 (14.7)
F	9.5 (2.5)	8.89 (2.35)	14.47 (31.9)	3,310 (7.30)	1010 (1850)	1040 (1900)	121	2.4	2.8	60	399 (14.1)

---

a/ Actual toxaphene content of the ~ 20% toxaphene dust formulation. The concentration ranged from 16.7 to 23.6%.

b/ The flame temperature was observed at a point approximately 15 cm (6 in.) in from the front wall of the incinerator (see Figure B-1).

c/ Calculated according to Method 3 of "Standards of Performance for New Stationary Sources," Federal Register, 36(247):24876-24895, 23 December 1971.

d/ Retention time is defined as $\frac{V}{v}$, where v is the wet off-gas flow rate from the incinerator at the respective chamber temperature and pressure, and V is the volume of that chamber.

e/ As dry gas at one atmosphere pressure, and 21.1°C (70°F).

Table 64. RESIDUE AND OFF-GAS CHARACTERISTICS--20% TOXAPHENE DUST EXPERIMENTS

	Feed rate		Solid residue				
			Primary chamber		Second chamber		
Run No.	20% Toxaphene formulation kg/hr (lb/hr)	Contained toxaphene[a] g/hr	Total kg/hr (lb/hr)	Chlorinated hydrocarbons[b] content ppm	Total kg/hr (lb/hr)	Chlorinated hydrocarbons[b] content ppm	Ratio of total incinerator residue to total charge
A	14.92 (32.9)	3,520	3.26 (7.2)	0.14	1.72 (3.8)	0.27	0.34
B	16.47 (36.3)	2,750	4.58 (10.1)	0.02	1.09 (2.4)	0.15	0.34
C	18.42 (40.6)	3,060	6.71 (14.8)	0.04	1.18 (2.6)	0.04	0.43
D	18.51 (40.8)	3,850	5.71 (12.6)	0.07	1.27 (2.8)	0.03	0.38
E	16.51 (36.4)	3,430	6.26 (13.8)	0.03	2.27 (5.0)	0.01	0.51
F	14.47 (31.9)	3,310	5.17 (11.4)	0.02	2.13 (4.7)	0.03	0.51

Run No.	Chlorinated hydrocarbons[b] content of off-gas g/hr	Chlorinated hydrocarbons[b] content of solid residues g/hr	Total chlorinated hydrocarbon[b] content of off-gas and solid residues g/hr	Ratio of total chlorinated hydrocarbons[b] in the off-gas to total toxaphene fed	Incineration efficiency[c] %
A	1.1×10^{-2}	9×10^{-4}	1.2×10^{-2}	3.1×10^{-6}	> 99.99
B	5×10^{-3}	2.5×10^{-4}	6×10^{-3}	2.0×10^{-6}	> 99.99
C	1.1×10^{-1}	3.1×10^{-4}	1.1×10^{-1}	3.6×10^{-5}	> 99.99
D	7×10^{-3}	4.4×10^{-4}	7×10^{-3}	1.8×10^{-6}	> 99.59
E	5×10^{-3}	2.1×10^{-4}	6×10^{-3}	1.6×10^{-6}	> 99.99
F	1.0×10^{-1}	1.7×10^{-4}	1.0×10^{-1}	3.0×10^{-5}	> 99.99

---

[a] Actual toxaphene content of the formulation.

[b] Total chlorinated hydrocarbon species detected.

[c] Efficiency is defined as: $\left[1 - \frac{\text{Quantity out}}{\text{Quantity in}}\right] \times 100$, where quantities of chlorinated hydrocarbons out is evaluated at Sample Points Nos. ② (incinerator off-gas) and ③ (solid residues). The [illegible]ty of toxaphene in is evaluated at Sample Point No. ① (incinerator feed).

Table 65. OFF-GAS COMPOSITION--20% TOXAPHENE DUST INCINERATION[a]

				Total hydrocarbon analyzer			Orsat analyzer			
Run No.	Chlorinated hydrocarbons[b] mg/m^3	SO_2 mg/m^3	NO_x[e] mg/m^3	Total hydrocarbons ppm	CO ppm	CH_4 ppm	O_2 vol. %	CO_2 vol. %	CO vol. %	Moisture vol. %
A	5.6×10^{-2}	299	74	78	> 5,340[f]	18	10.5	8.3	0.2	8.4
B	1.9×10^{-2}	NA[c]	NA	46	4,530	5	13.3	6.1	0.1	8.6
C	3.3×10^{-1}	ND[d]	ND	NA	NA	NA	7.6	10.3	0.1	7.0
D	2.4×10^{-2}	< 1	1	20	105	2	7.2	9.5	1.1	8.1
E	1.3×10^{-2}	3	28	18	ND	2	11.8	6.6	0.0	6.8
F	2.5×10^{-1}	97	6	< 1	176	7	11.9	6.8	0.0	8.2

---

[a] As dry gas at one atmosphere pressure, and 21.1°C (70°F).
[b] Total chlorinated hydrocarbon species detected.
[c] No analysis.
[d] Not detected.
[e] Calaculated as NO_2.
[f] Upper detection limit.

Table 66. PARTICULATE SAMPLING SUMMARY--20% TOXAPHENE DUST EXPERIMENTS

Description	A	B	C	D	E	F
Vol. dry gas - std. cond., nm^3	0.321	0.444	0.319	0.427	0.659	0.644
Percent moisture by vol.	8.4	8.6	7.0	8.1	6.8	8.2
Avg. stack temperature, °C	195.6	194.0	259.5	271.8	363.0	330.1
Stk. flow rate, dry., std. cond., nm^3/min	3.0	4.3	5.2	4.3	6.5	6.1
Actual stack flow rate, m^3/min	5.2	7.5	10.1	8.5	15.1	13.7
Percent isokinetic	102.4	98.7	116.6	96.0	97.3	100.8
Percent excess air	96	166	54	44	124	125
Particulates - partial catch						
Particulate wt. - partial, mg	10,700	8,230	1,240	2,570	873	2,780
Part. load - ptl., std. cn., mg/nm^3	33,100	18,500	3,890	6,010	1,320	4,310
Part. load - ptl., stk. cn., mg/m^3	19,000	10,700	2,020	3,000	567	1,920
Partic. emis. - partial, kg/hr	5.959	4.772	1.223	1.533	0.513	1.580
Particulates - total catch						
Particulate wt. - total, mg	16,400	8,270	1,270	2,660	958	2,880
Part. load - ttl., std. cn., mg/nm^3	50,800	18,600	3,960	6,230	1,450	4,460
Part. load - ttl., std. cn., corrected to 12% CO_2, mg/nm^3	73,000	37,000	4,620	7,900	2,640	7,900
Part. load - ttl., stk. cn., mg/m^3	29,200	10,700	2,060	3,110	622	1,990
Partic. emis. - total, kg/hr	9.142	4.800	1.247	1.590	0.564	1.636
Percent impinger catch	34.81	0.58	1.91	3.55	8.95	3.45

Table 67. OPERATIONAL DATA SUMMARY--60% TOXAPHENE DUST EXPERIMENTS

Run No.	A	B	C	D	E	F
Temperature °C (°F)						
Primary chamber (Thermocouple No. ①)	640 (1180)	640 (1180)	970 (1780)	1010 (1850)	930 (1710)	990 (1820)
Primary chamber (Thermocouple No. ②)	550 (1020)	560 (1040)	990 (1810)	1030 (1880)	910 (1670)	990 (1810)
Primary chamber (Thermocouple No. ③)	670 (1240)	670 (1240)	1010 (1850)	1030 (1880)	970 (1770)	1010 (1850)
Second chamber (Thermocouple No. ④)	560 (1040)	580 (1070)	850 (1570)	850 (1570)	820 (1500)	840 (1540)
Second chamber (Thermocouple No. ⑤)	370 (700)	380 (710)	570 (1050)	500 (930)	510 (950)	510 (950)
Sample Point No. ② (Thermocouple No. ⑥)	190 (380)	240 (460)	280 (530)	290 (560)	380 (710)	370 (690)
Pressures						
Draft (Manometer No. △1), pascals (in. H_2O) gauge	16 (0.065)	26 (0.105)	32 (0.130)	32 (0.130)	52 (0.210)	50 (0.200)
Burner operation pressure, pascals (psi) gauge	7.6×10^5 (110)	7.6×10^5 (110)	7.6×10^5 (110)	7.6×10^5 (110)	9.3×10^5 (135)	9.3×10^5 (135)
Pesticide injection air, pascals (psi) gauge	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)

The efficiency of combustion has been calculated on the basis of total chlorinated hydrocarbons in the off-gas and solid residues versus the toxaphene injected into the incinerator. The efficiency of toxaphene incineration for all six tests was > 99.99%. Inclusion (or exclusion) of the chlorinated hydrocarbons content of the solid residues left in the primary and secondary chambers of the incinerator is too small to change the above percent efficiency.

An unusually high level of chlorinated hydrocarbon was reported in the liquid nitrogen trap in the Sample Point No. ② sample train from Run No. F. In fact, the amount of chlorinated hydrocarbons reported in this trap for Run No. F were more than 50 times that of the next highest value. Thus, it seems probably that the high chlorinated hydrocarbon level shown for the off-gas from Run No. F is the result of a contaminated sample. The results of Run No. C, as discussed below, are also somewhat suspect.

Particulate sampling results are summarized in Table 66. All runs with the exception of C were within acceptable isokinetic limits. The dust formulations of toxaphene have followed the previously established trend of high particulate emission levels for dust formulations. The incineration of toxaphene dust formulation will require a particulate emissions control system to meet established limits.

Runs A and B have grain loadings considerably higher than the remainder of the toxaphene dust series. This was partly the result of the production of an oily material which was collected in the impingers and cryogenic trap of the sampling train. The source of this material is unknown, but it is possible that it is the result of poor combustion of the supplementary fuel. It has been determined that the oil does not contain chlorinated hydrocarbons.

Operating difficulties were encountered on all four tests made at the higher temperature of ~ 1000°C (1830°F), i.e., Runs C through F. In fact, Run No. C was terminated when only half completed (30 min of sampling) because of loss of draft within the incinerator. Inspection of the incinerator disclosed that the six 11.4 cm x 11.4 cm (4-1/2 in. x 4-1/2 in.) openings in the wall between the primary and secondary chamber (see Figure 2, p. 22) had been completely plugged. The interior of the "plugged incinerator" is shown in Figure 44. During the remaining tests (Runs Nos. D, E, and F) the three lower openings were kept open by means of periodic clearing with a rod inserted through the view port in the front wall of the primary chamber.

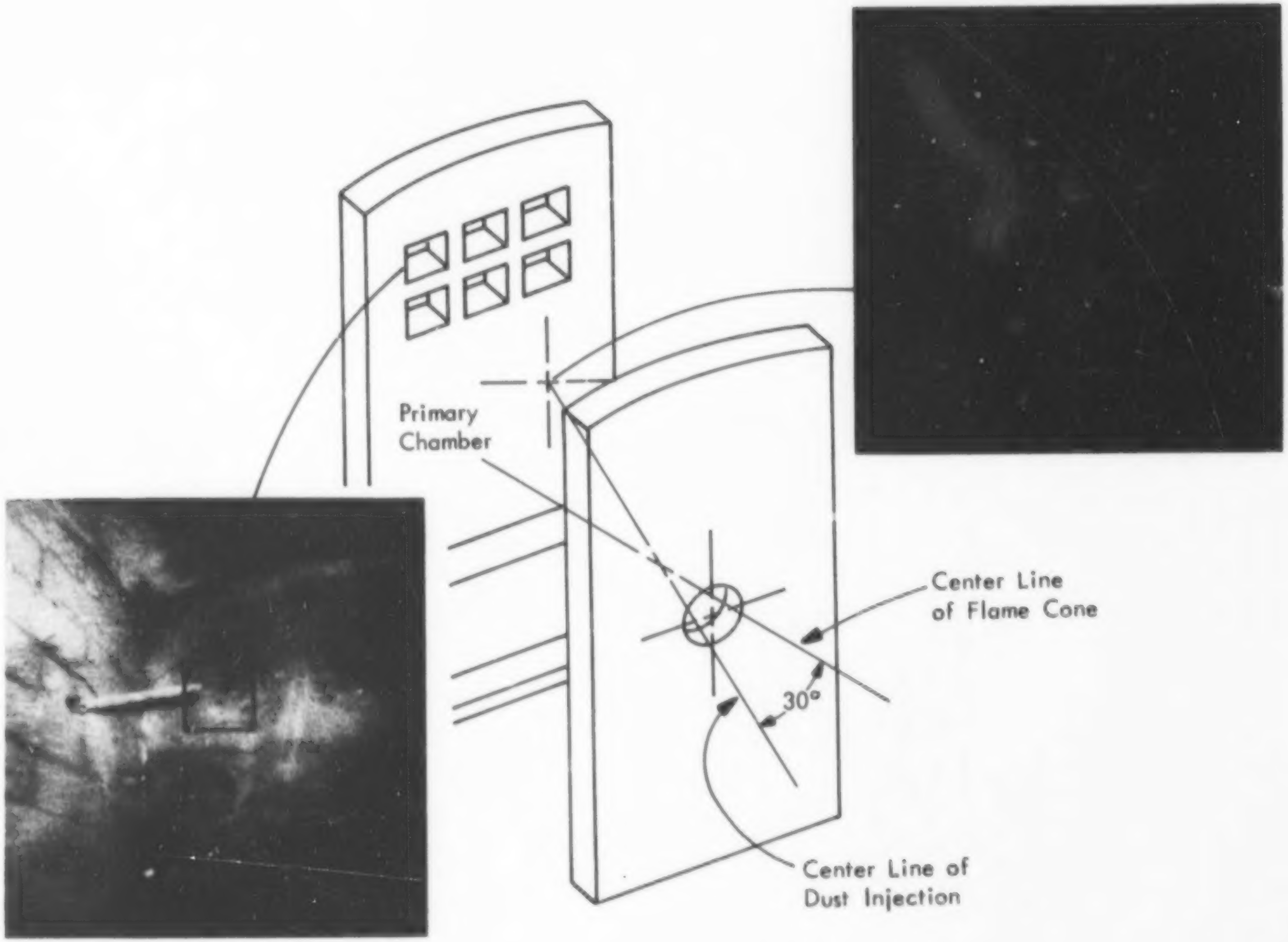


Figure 44. Interior of plugged incinerator

Upon completion of the tests with toxaphene, the experimental apparatus was inspected for any deposits or residues of pesticide containing materials. Scrapings from the wall of the horizontal section of the incinerator stack, the bottom of the first water scrubber, and the demister pad in the first water scrubber contained 0.05, 0.17, and 2.3 ppm of chlorinated hydrocarbons, respectively. Wall scrapings from the vertical section of the incinerator stack contained 0.2 ppm of chlorinated hydrocarbons. Thus, there was apparently no significant deposition of chlorinated hydrocarbon compounds in the experimental apparatus.

DISCUSSION

Problems were encountered with the feeding as well as with the incineration of the 20% dust formulation. The dust tended to bridge in the feed line to the injection nozzle upstream of the point of air injection (see Appendix A for details of the dust injection system).

As has already been pointed out, plugging of the checker work between the primary and secondary chambers when operating at the higher temperature was a major problem.

Bridging problems have been encountered by others using dust formulations using attapulgite clay as the inert carrier; grounding of the screens overcame the difficulty, indicating that a static electrical charge on the dust particles was the cause.[4] It is quite possible that static charges contributed to the toxaphene dust plugging problems. The "whiskering" effect shown in the residue (see Figure 44) tend to support this theory.

References

1. Casida, J. E., R. L. Holmstead, S. Khalifa, J. R. Knox, T. Ohsawa, K. J. Palmer, and R. Y. Wong, "Toxaphene Insecticide: A Complex Biodegradable Mixture," Science, 183:520-521 (8 February 1974).

2. Metcalf, R. L., Organic Insecticides, Interscience Publishers, New York, New York (1955).

3. von Rümker, R., E. W. Lawless, and A. F. Meiners, "Production, Distribution, Use and Environmental Impact Potential of Selected Pesticides," Final Report, Contract No. EQC-311, for Council on Environmental Quality, Washington, D.C. (1974).

4. Bell, W. L., Consultant, Arlington Blending and Packaging Co., Personal Communication to Mr. Thomas L. Ferguson (10 April 1975).

VI. ATRAZINE

PESTICIDE DESCRIPTION

Physical Properties

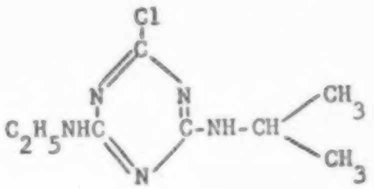
Chemical Name: 2-Chloro-4-ethylamino-6-isopropylamino-S-triazine

Common Name: Atrazine

Trade Names: Atranex®, AAtrex®, Gesaprim®, G-30027, Primatol A®, Atra-Bor®, Atratol®

Pesticide Class: Herbicide

Structural Formula:



Empirical Formula: $C_8H_{14}ClN_5$

Molecular Weight: 215.7

Physical State: Colorless crystals

Melting Point: 173 to 175°C

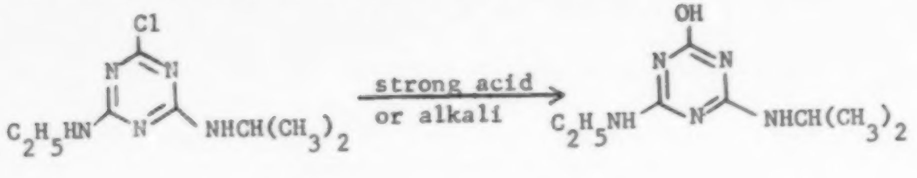
Vapor Pressure: 3.0×10^{-7} mm Hg at 20°C

Solubility:

Solvent	Temperature C	Solubility (ppmw)
Dimethyl sulfoxide	27	183,000
Chloroform	27	52,000
Ethyl acetate	27	28,000
Methanol	27	18,000
Diethylether	27	12,000
N-Pentane	27	360
Water	27	33

Chemical Properties

Atrazine is reportedly hydrolyzed by either acid or base as shown:[1/]



Putnam et al.[2/] reported that > 99% of atrazine underwent decomposition when burned in polyethylene or multiwall Kraft bags (a 0.5 g atrazine sample).

Production and Use

Atrazine is the most widely used herbicide in the United States. Major crops on which it is used are corn, sorghum and sugarcane; minor uses include nonselective control. The estimated 1972 domestic consumption was 75 million pounds (von Rümker et al.[3/]).

Available formulations include an 80% wettable powder, and a 4 lb/gal flowable concentrate. Atrazine is also formulated in combination with other active ingredients including propachlor, amitrole, and fenac.

FORMULATIONS TESTED

The two principal atrazine formulations, the 80% wettable powder and the 4 lb/gal flowable concentrate, were tested.

4 Lb/Gal Flowable Concentrate

Name: AAtrex® 4L Herbicide

Manufacturer: Agricultural Division, CIBA-GEIGY Corporation,
Greensboro, North Carolina

Composition:	Active Ingredients	43%
	Atrazine (2-chloro-4-ethylamino-6-isopropylamino-S-triazine)	40.8%
	Related Compounds	2.2%
	Inert Ingredients	57%
	Total	100.0%

Registration: EPA Reg. No. 100-497 AA

80% Wettable Powder

Name: AAtrex® 80W Herbicide

Manufacturer: Agricultural Division, CIBA-GEIGY Corporation, Greensboro, North Carolina

Composition: Active Ingredients		80%
Atrazine (2-chloro-4-ethylamino-6-isopropylamino-S-triazine)	76%	
Related Compounds	4%	
Inert Ingredients		20%
Total		100%

Registration: EPA Reg. No. 100-439ZA

Particle Size Specifications: Formulated on kaolinite clay such that a maximum of 0.02% is larger than 297 μ, and a maximum of 3.0% larger than 44 μ.

PRELIMINARY THERMAL ANALYSIS

Bomb calorimetric analysis of atrazine gave the following results.

Sample	Test	Test Method	Result
Liquid formulation[a]	Sulfur	ASTM D-129	0.77%
	Calorific value	ASTM D-2015	2.471×10^7 J/kg (10,634 Btu/lb)
80% wettable powder	Sulfur	ASTM D-129	0.96%
	Calorific value	ASTM D-2015	2.020×10^7 J/kg (8,692 Btu/lb)
Technical grade	Sulfur	ASTM D-129	0.69%
	Calorific value	ASTM D-2015	2.328×10^7 J/kg (10,018 Btu/lb)

---

[a] The liquid was oven-dried and the analysis performed on the residue.

Figures 45 and 46 show the results of DTA and TGA of the technical grade atrazine. DTA data show that decomposition of the compound starts at about 180°C with two distinct endotherms at about 185 and 240°C, and exotherms at about 350, 450, and 470°C. The decomposition process is substantiated by the TGA data which indicate that almost 95% of the sample weight is lost at about 300°C, and at about 600°C, no sample is left.

Figures 47 and 48 show the results of DTA and TGA of a sample of atrazine obtained by evaporation of a sample of the liquid formulation. DTA data show that as temperature increases decomposition of the sample starts, and at about 185 and 245°C, two prominent endotherms are observed. As temperature reaches to about 350 and 440°C, respectively, distinct exotherms are observed. The decomposition process is again substantiated by the TGA data which show that from 200 to 220°C about 90% of the sample is lost, and at about 600°C, practically all the sample is gone.

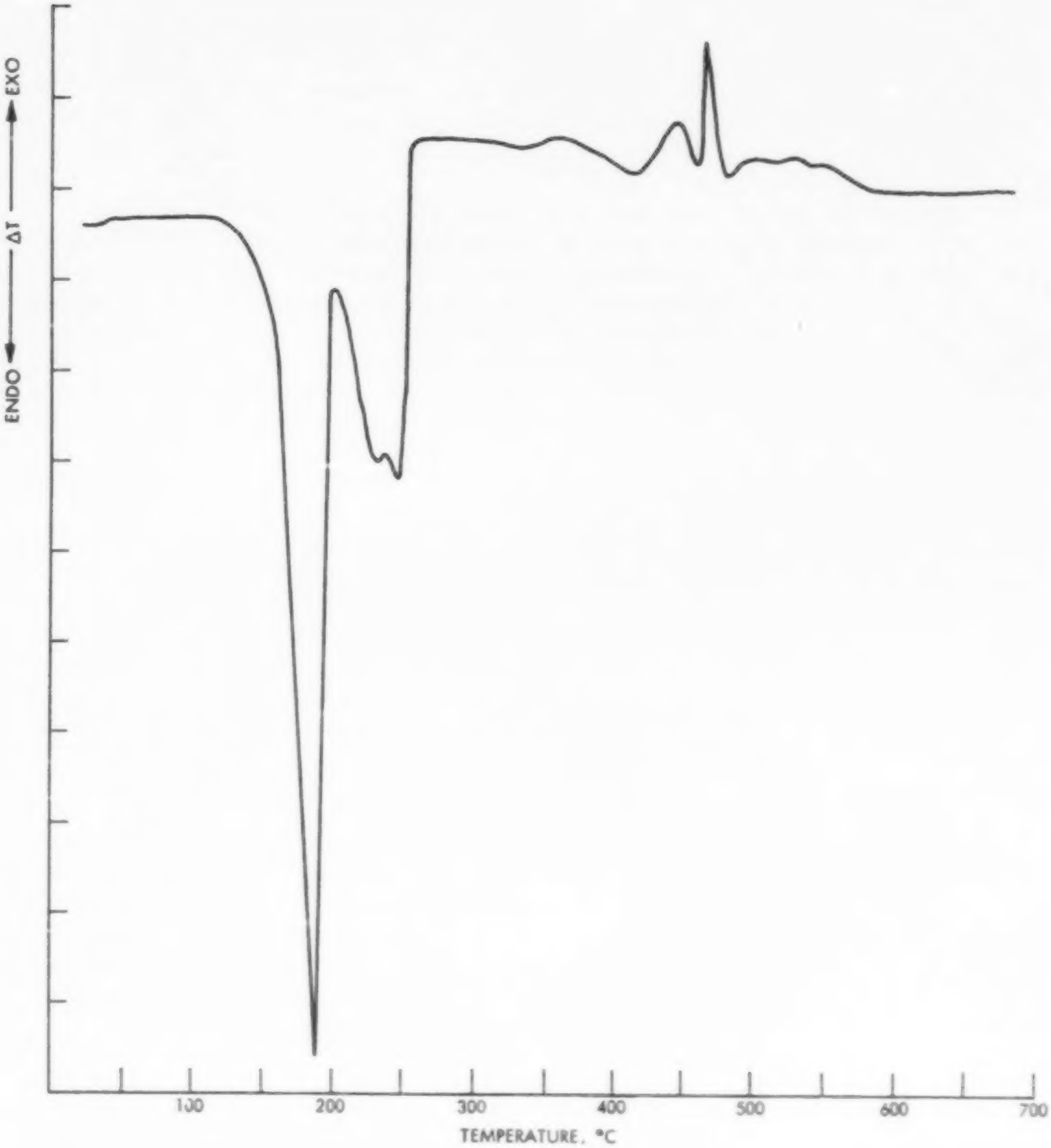
Figures 49 and 50 show the results of DTA and TGA data of atrazine wettable powder formulation. DTA data show that, aside from the familiar pattern of endotherms (at 185 and 225°C) and exotherms (at 350 and 550°C), additional endotherms and exotherms are observed. These endotherms and exotherms could very well be attributed to the additives in the dust formulation. The decomposition is completed at about 600°C. This is substantiated by TGA data which show that at 600°C over 90% of the sample is gone.

Kennedy et al.[4/] also conducted DTA analysis of atrazine. The results of their analyses were as follows:

	Endotherms	Exotherms
Reference Standard	210, 308, 334, 360, 400 and 480°C	290, 385, and 582°C
80% Wettable Powder Formulation	182 and 280°C	250, 315, and 550°C

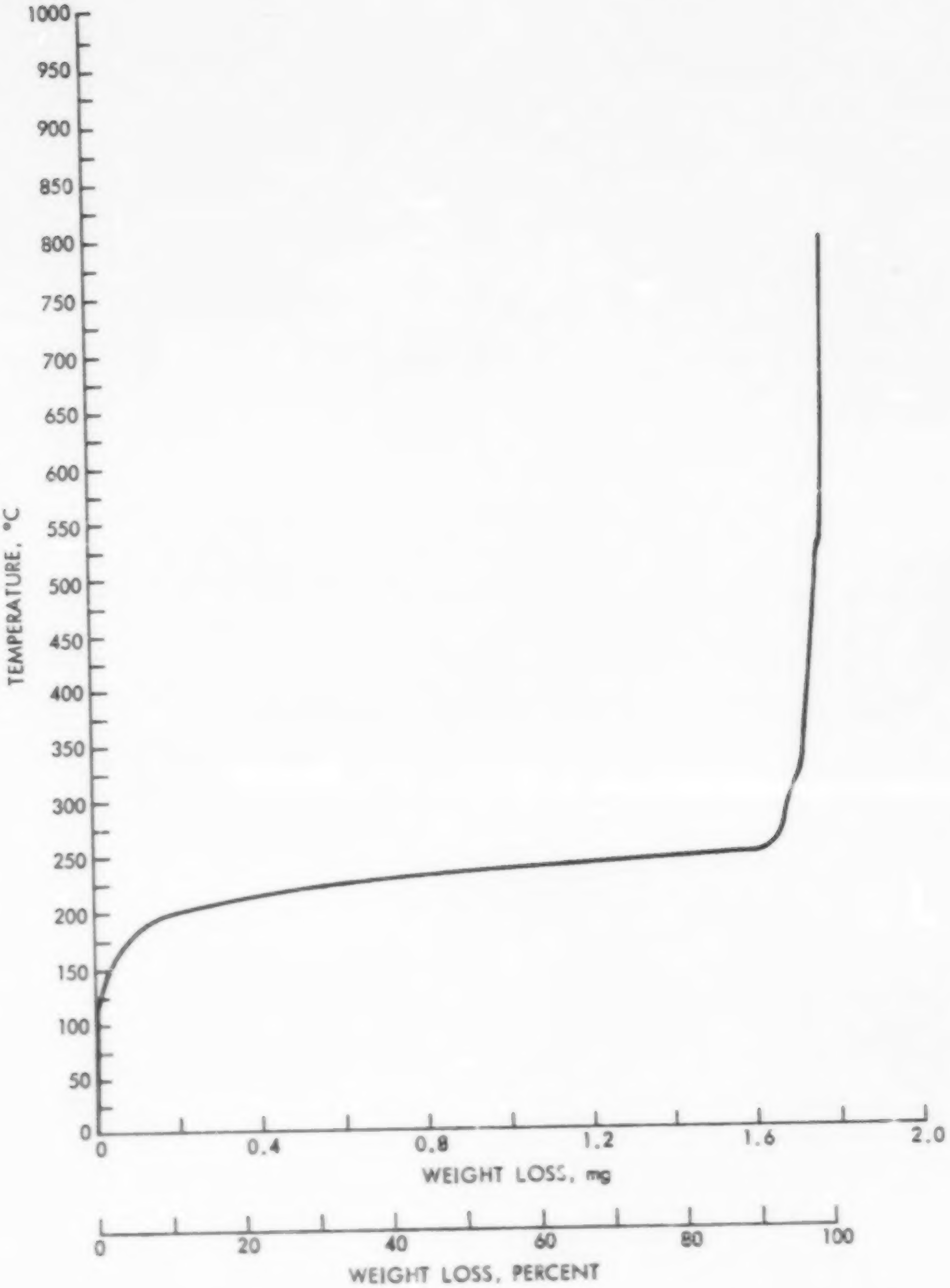
Sensitivity = 25%

Based on these and other laboratory analyses, Kennedy et al. concluded that the temperatures of complete combustion of the atrazine reference standard and the 80% wettable powder formulation were 650°C (1202°F) and 600°C (1112°F), respectively.



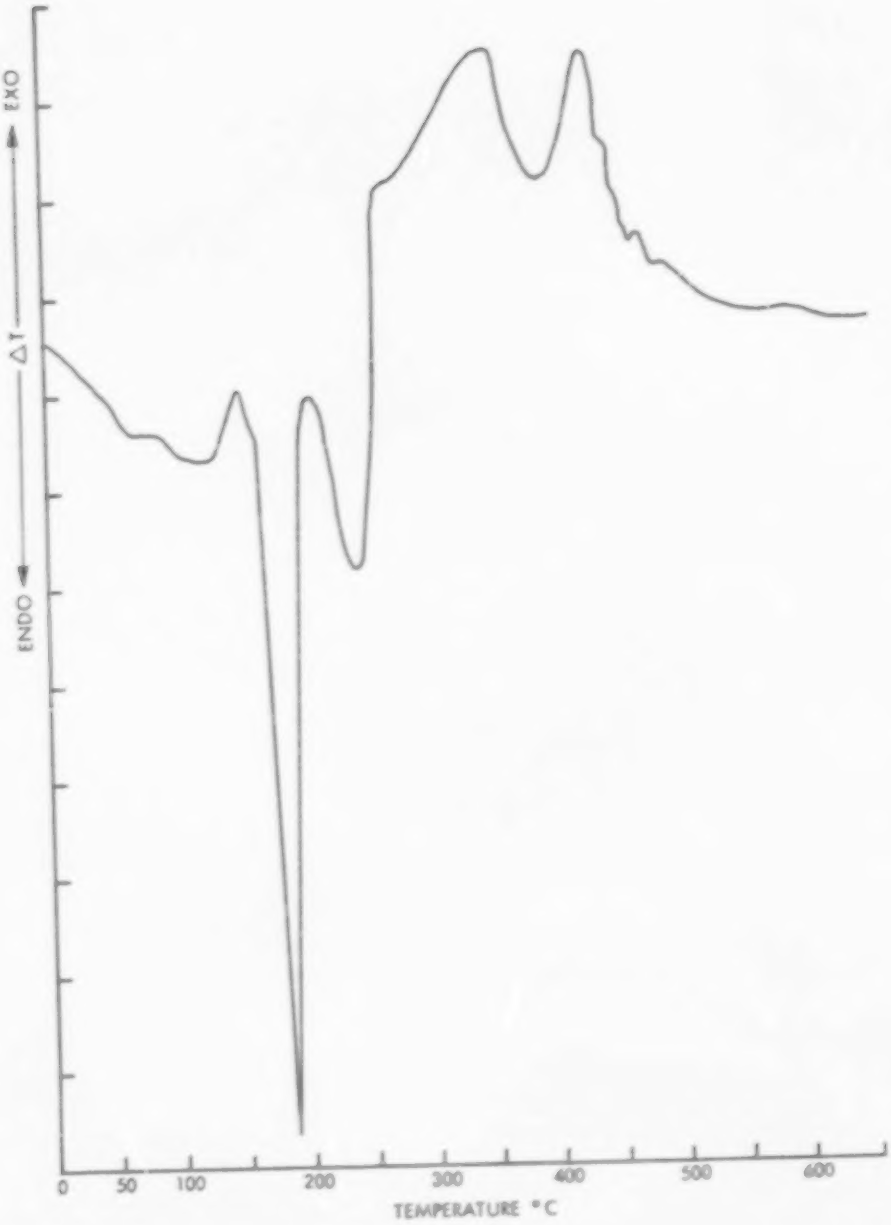
Reference: Al_2O_3 + Kaolinite
Prog. mode: Heat
Rate: 20°C/min

Figure 45. DTA of technical atrazine.



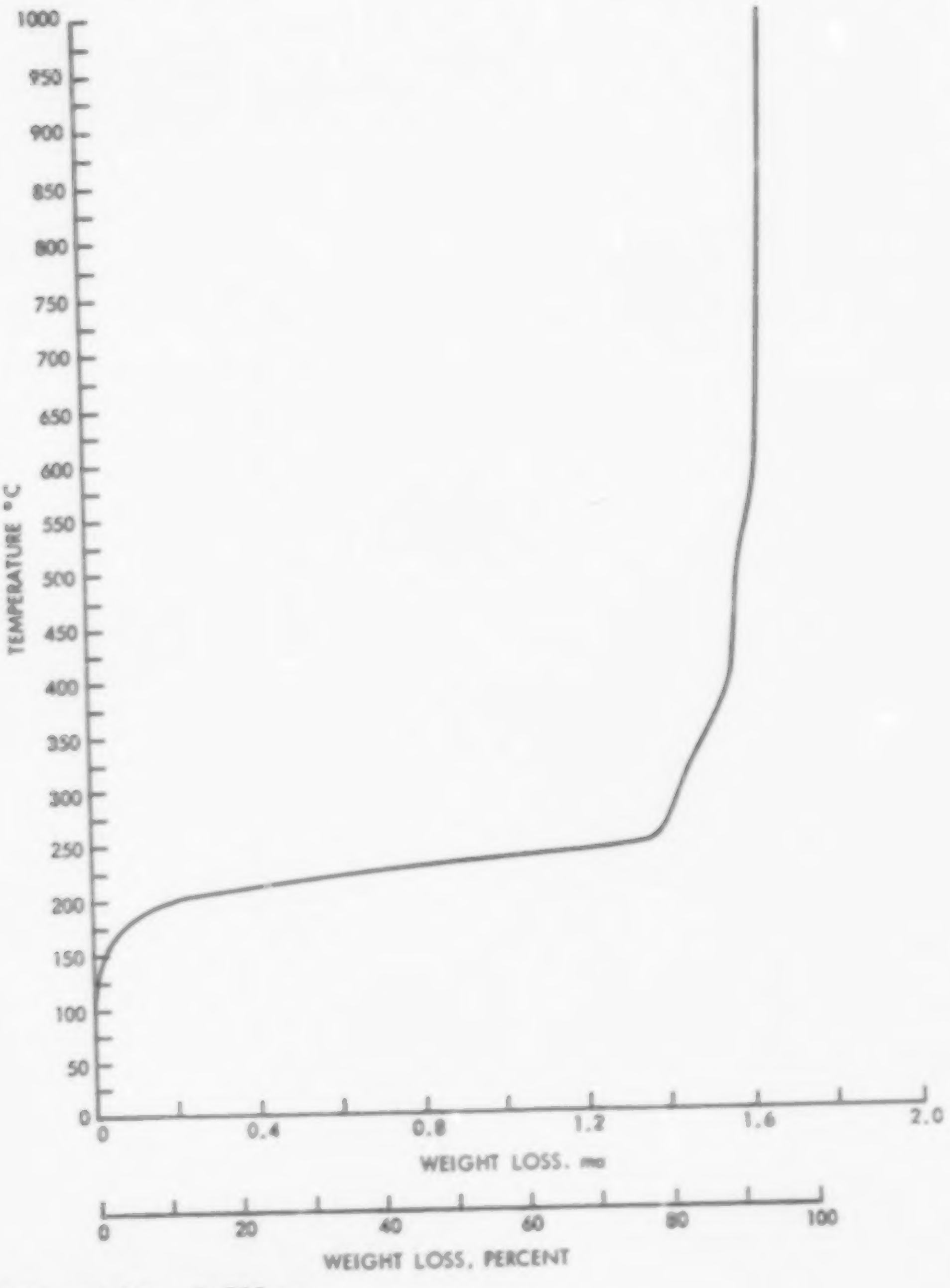
Sample weight: 1.764 mg
Heating rate: 20°C/min
Environment: ~ 20 ml/min air (20% O_2, 80% N_2)

Figure 46. TGA of technical atrazine.



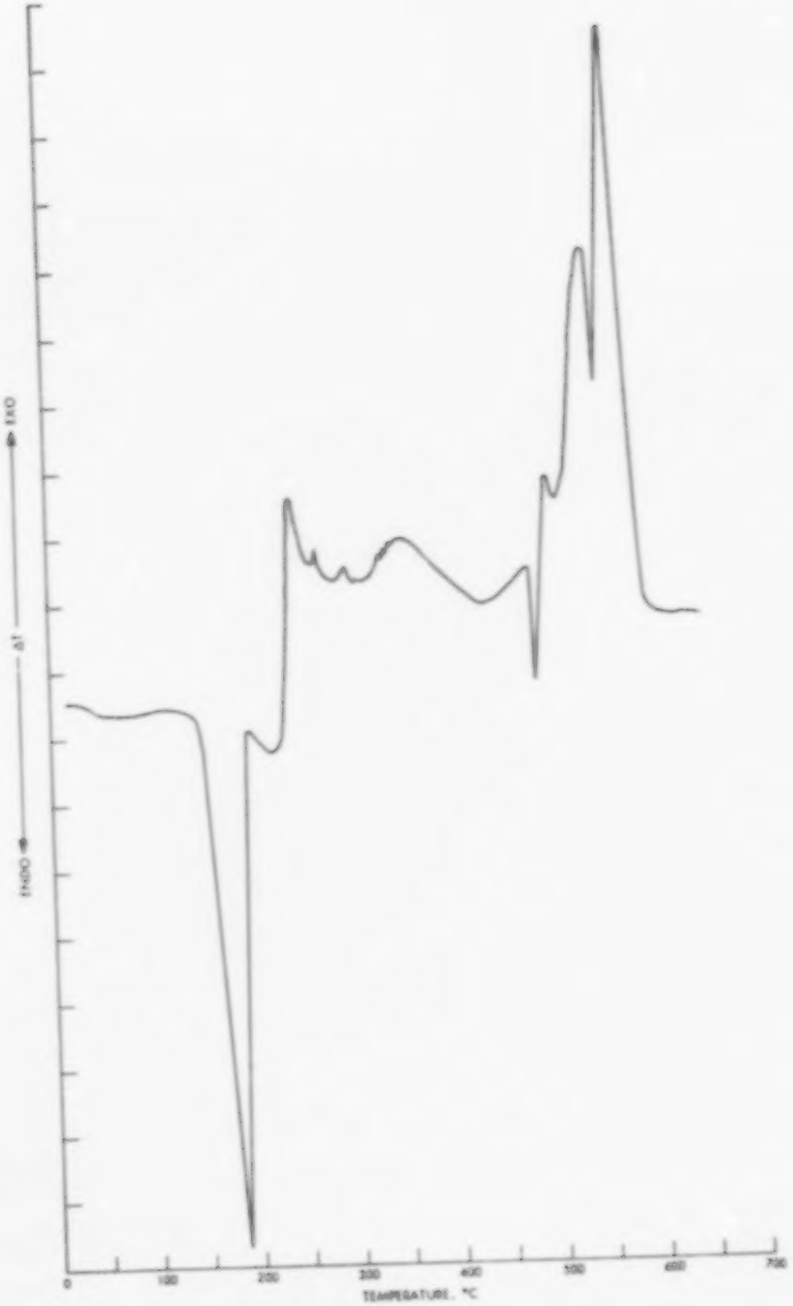
Reference: Al_2O_3 + Kaolinite
Prog mode: Heat
Rate: 20°C/min

Figure 47. DTA of dried liquid atrazine formulation.



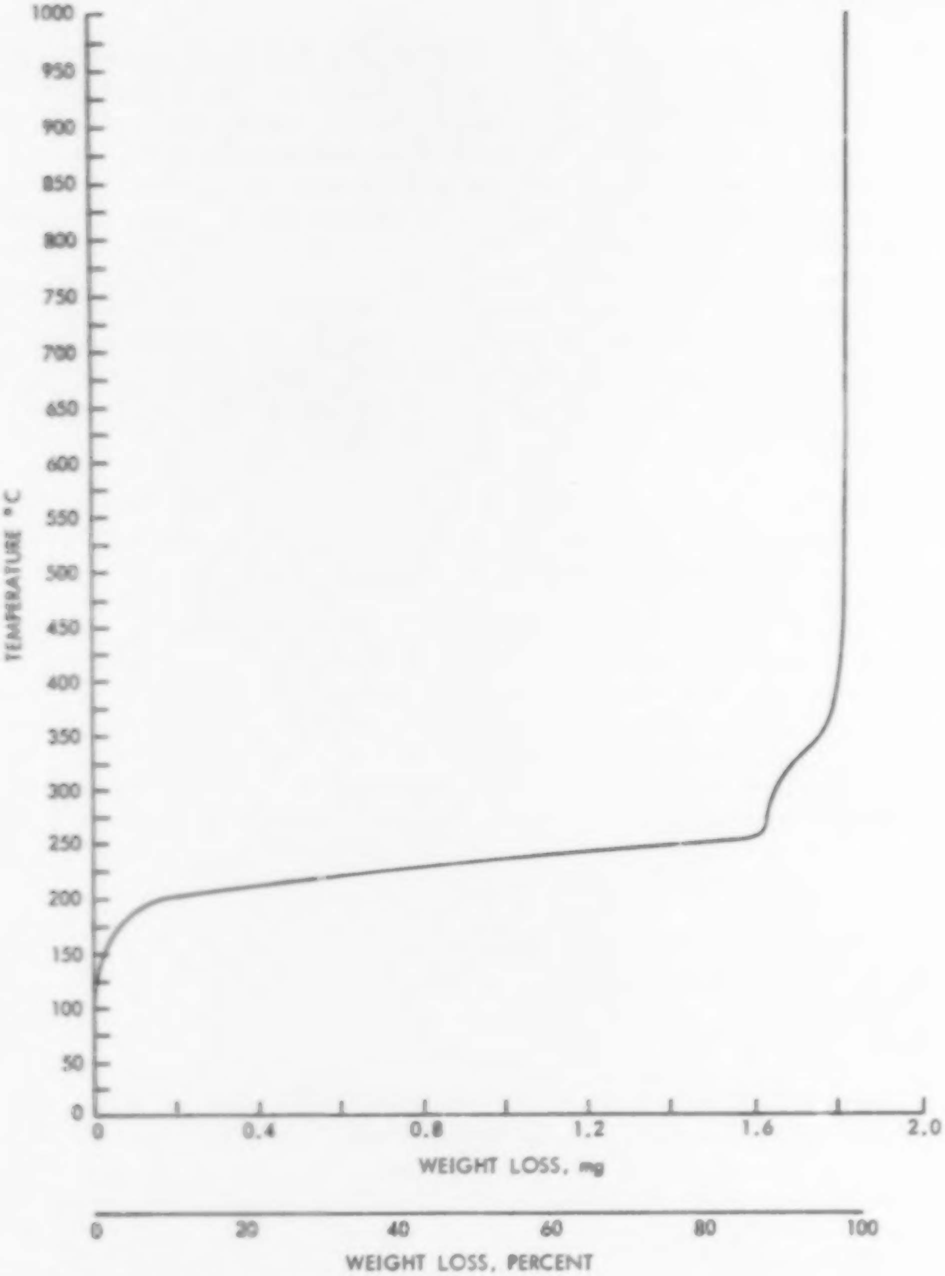
Sample weight: 1.866 mg
Heating rate: 20°C/min
Environment: ~ 20 ml/min air (20% O_2, 80% N_2)

Figure 48. TGA of dried liquid atrazine formulation.



Reference: Al_2O_3 + Kaolinite
Prog mode: Heat
Rate: 20°C/min

Figure 49. DTA of ~ 80% atrazine wettable powder.



Sample weight: 1.854 mg
Heating rate: 20°C/min
Environment: ~ 20 ml/min air (20% O_2, 80% N_2)

Figure 50. TGA of ~ 80% atrazine wettable powder

METHODS OF ANALYSIS

Direct gas chromatographic analysis of atrazine with electron capture detector is not feasible due to the low response of single chlorine atom in the atrazine molecule. In addition, atrazine's major metabolite, hydroxyatrazine, is not detectable by electron capture. However, the hydrogens attached to the nitrogen atoms (of atrazine and hydroxyatrazine) and the hydroxyl group in hydroxyatrazine should be susceptible to acylation. Therefore, halogenated-acyl derivatives can be formed by using a reagent, such as N-heptafluorobutyrylimidazole, to form derivatives suitable for electron capture detection. This procedure, as reported in the literature, will improve the response of atrazine and hydroxyatrazine to electron capture detection 10-fold to 100-fold. Three halogenated reagents, pentafluorobenzoyl chloride, N-heptafluorobutyrylimizole, and 4-chloro-3-nitro-benzotrifluoride were evaluated for use.

This method was successfully applied to standard atrazine solutions. Efforts to adapt this technique to the analysis of incinerator effluent samples, however, were not successful.

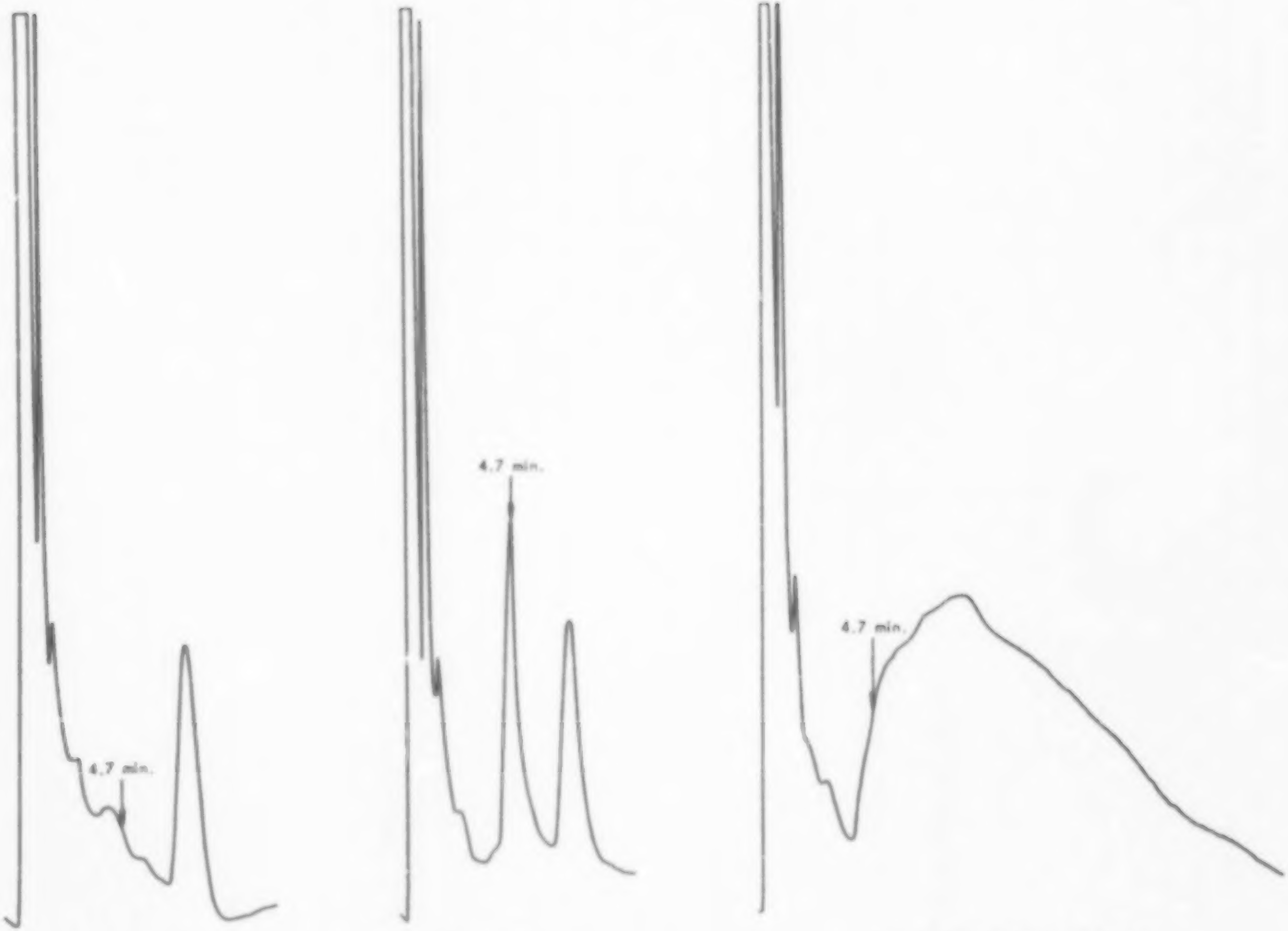
Figures 51a and 51b show a blank and a 10.9 mg atrazine solution, respectively. The peak eluted at 4.7 min in Figure 51b is derivated atrazine. However, when this method was applied to a series of representative incinerator effluent samples in which residual atrazine was most probably present, chromatograms showed a relatively high background plus a broad peak that covered the area where atrazine is expected to elute. Figure 51c shows the chromatogram of a representative incinerator effluent gas sample from a liquid atrazine formulation test. Analysis of atrazine by this method, therefore, was not feasible.

An alkaline flame detector was obtained in order to allow more accurate analysis of the atrazine samples.

Apparatus

A Perkin-Elmer 3920 gas chromatograph equipped with a phosphorus-nitrogen thermionic detector (bead setting 500, polarizing voltage X3) and a 6 ft, 2 mm I.D. stainless steel column (packed with 1.5% OV-17 + 1.95% QF-1 on 100/120 mesh Supelcoport from Supelco, Inc., Bellefonte, Pennsylvania) was used for gas chromatographic analysis. Chromatographic operating conditions were: injector and detector temperature, 235°C; column temperature, 200°C; flow rate, 40 ml/min, He; detector gas flow rates, 6 ml/min, H_2 and 75 ml/min, air.

A Perkin-Elmer No. 56 strip chart recorder was used to record the chromatograms.



a. Derivatized Blank

b. Derivatized Atrazine

c. Derivatized Incinerator Sample

Figure 51. Representative atrazine chromatograms

Reagents and Materials

Solvents used were pesticide grade benzene (Fisher Scientific) for all samples (except the hexylene glycol from the second stage scrubber) and all standard solutions; and reagent grade methanol (Fisher Scientific) for initial extraction of the Sample Point No. ② train, and to prepare solutions of hexylene glycol. (Note that pesticide grade solvents are not absolutely imperative because of the high specificity of the phosphorus-nitrogen thermionic detector.) All laboratory glassware (vials, beakers, pipettes, etc.) was washed with Alconox detergent (Scientific Products) and rinsed with deionized distilled water water and reagent grade acetone (Fisher Scientific).

Standard and Calibration Curves

The atrazine standard, obtained from USEPA, was used to prepare a stock solution of 27.2 μg/ml atrazine, from which appropriate dilutions were made to produce linear results (linear range utilized: subnanogram to 1 μg atrazine).

Procedure for Sample Preparation

The mass of collected particulates was determined for the incineration of solid atrazine as follows. All samples were taken to dryness in clean, dessicated, tared 250 ml beakers and were dessicated 2 days before final weighing. The residue was extracted with methanol and this was taken just to dryness and tightly capped. The methanol extract from the silica gel and all other solutions, as well as liquid samples collected from incineration of atrazine liquid formulation (except the hexylene glycol from the second stage scrubber) were taken to dryness in the French Squares bottles as received. One milliliter each of the hexylene glycol samples was pipetted into vials and made up to 10 ml with methanol. These samples were run directly and all other impinger, blank and wash samples were taken up in appropriate amounts of benzene just prior to gas chromatographic analysis. Some samples with heavy particulate interference were filtered and taken just to dryness again; the filter and particulate matter was washed thoroughly with benzene after filtration of the sample itself.

Portions of all cleanout samples (primary chamber, secondary chamber, etc.) were weighed out and extracted and the extracts were analyzed for atrazine.

Analysis and Discussion

All samples were analyzed for atrazine. Unidentified chromatographic peaks were quantitated against the atrazine calibration curve.

The sensitivity of the instrument for atrazine is 300 pg. Based on this sensitivity, and with a 5-μl sample injection for each analysis, the minimum detectable value for a 20-ml sample solution is 1.2 μg. However, during the analysis, samples were concentrated down to 1 ml, which resulted in a minimum detectable quantity of 60 ng.

The first step in method development for atrazine analysis involved an attempt to derivitize atrazine with three halogenated reagents, namely pentafluorobenzol chloride, 4-chloro-3-nitro-benzotrifluoride, and N-heptafluorobutyrylimidazole, and subsequent analysis with electron-capture GC. Interferences were encountered due to large number of peaks from nonnitrogen-containing materials in the samples and the reagents. Furthermore, no methods were available in the literature dealing with nanogram to subnanogram levels of detection of atrazine without extensive sample cleanup.

After the delivery of the Perkin-Elmer instrument, extensive time was spent to obtain optimum instrumental parameters for the analysis of atrazine in the incineration samples with minimum sample clean-up.

TEST CONDITIONS AND RESULTS

Nine tests were conducted using the 4 lb/gal liquid formulation of atrazine. An additional five tests were conducted using an 80% wettable powder formulation of atrazine in order to evaluate the effect of physical form on the efficiency of atrazine incineration.

Nominal operating conditions for these tests were "high" and "low" feed rates 3.40 kg ((7.5) and 1.70 kg (3.75 lb) active ingredient/hr), excess air rates (150 and 50%), and operating temperatures, 1000°C (1830°F) and 650°C (1200°F). These operating temperatures were based on DTA and TGA of atrazine samples which indicated that this pesticide could be expected to decompose at a temperature of 650°C (~ 1200°F).

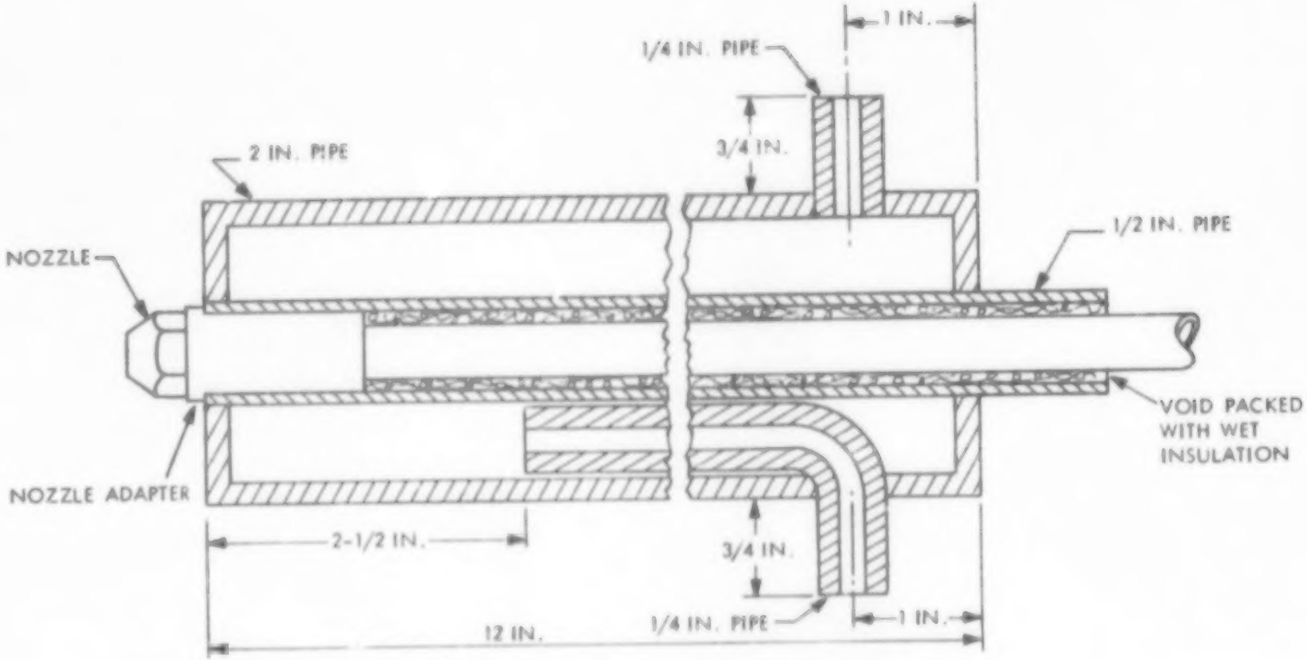
Liquid atrazine, like the water-based picloram formulation, is not miscible with No. 2 fuel oil, and therefore, was pumped into the incinerator using a separate injector system. The liquid atrazine injector system utilized standard fuel oil burner nozzles of the appropriate size, and the nozzle adapter and oil pipe from a fuel oil burner (Part Nos. 33 and 24, respectively, Figure 13, p. 95). Preliminary tests, however, showed that the liquid atrazine would plug the nozzle and nozzle adapter almost immediately after insertion into the incinerator chamber. For this reason, the nozzle adapter was modified so that it would be cooled by the water jacketed injection nozzle used for dust injection, as shown in Figure 52. This modification eliminated the problem of plugging during the test period.

Results of tests using the 4 lb/gal liquid formulation are given in Tables 68 through 71. Two efficiencies of combustion were calculated for the atrazine liquid tests, as defined in Table 69. The first was based on atrazine only, while the second included consideration of all nitrogenous organic species (including atrazine) detected in the effluent gas. Both of these efficiencies were > 99.99% for all tests. Thus, the efficiency of liquid atrazine incineration was found to be > 99.99% over the temperature range of 550°C (1030°F) to 1040°C (1900°F).

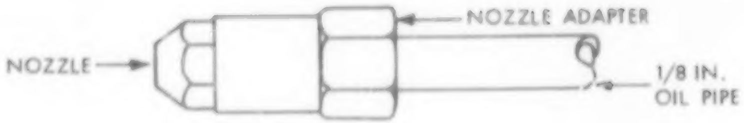
The relative quantity of atrazine (and total nitrogenous organic species) not decomposed, however, does appear to be related to operating temperature. The highest quantity of atrazine (and total nitrogenous organic species) as shown in Columns 3 and 5, respectively, of Table 69, was emitted from Run No. 6, which was conducted at the lowest primary chamber temperature (550°C). The lowest quantities detected were from Run No. 9, which was conducted at the highest temperature (1040°C).

Five additional tests were made using an 80% wettable powder formulation of atrazine in order to determine the effect of physical form on the efficiency. Operational data and analytical results for the ~ 80% atrazine wettable powder formulation tests are summarized in Tables 72 through 76. The results of these five tests parallel those of the nine tests using the liquid atrazine formulation. Both efficiencies for all five tests were > 99.99%.

The results of cyanide analysis for all 14 atrazine tests (nine liquid and five dust) are summarized on page 277.



B. MODIFIED, WATERCOOLED INJECTION NOZZLE



A. STANDARD BURNER NOZZLE

Figure 52. Liquid atrazine formulation injection system

Table 68. SUMMARY OF 40.8% ATRAZINE FLOWABLE CONCENTRATE EXPERIMENTS

	Fuel oil rate		Atrazine rate						Retention time sec[e]			
Run No.	Nominal burner size ℓ/hr (gal/hr)	Actual feed rate ℓ/hr (gal/hr)	Nominal nozzle size ℓ/hr (gal/hr)	Actual feed rate ℓ/hr (gal/hr)[a]	Atrazine rate g/hr (lb/hr)[b]	Primary chamber temperature °C (°F)	Flame temperature[c] °C (°F)	Excess air[d] %	Primary chamber	Second chamber	Sampling time min	Off-gas flow rate[f] m³/hr (1,000's of SCFH)
1	11.4 (3.0)	9.84 (2.60)	9.5 (2.5)	7.15 (1.89)	1,470 (3.25)	1020 (1860)	1070 (1960)	79	2.6	2.5	30	207 (7.3)
2	11.4 (3.0)	9.84 (2.60)	9.5 (2.5)	7.53 (1.99)	1,470 (3.25)	1020 (1860)	1130 (2060)	123	2.1	2.0	30	269 (9.3)
3	4.7 (1.25)	4.31 (1.14)	9.5 (2.5)	6.40 (1.69)	1,320 (2.92)	730 (1340)	1105 (2020)	138	6.0	3.6	30	181 (6.4)
4	3.8 (1.0)	3.33 (0.88)	9.5 (2.5)	7.15 (1.89)	1,600 (3.52)	700 (1290)	1080 (1980)	90	5.0	4.6	30	144 (5.1)
5	11.4 (3.0)	9.08 (2.40)	22.7 (6.0)	16.54 (4.37)	3,420 (7.56)	970 (1780)	1090 (1990)	76	2.0	1.8	30	272 (9.6)
6	2.8 (0.75)	2.73 (0.72)	22.7 (6.0)	16.09 (4.25)	3,410 (7.51)	550 (1030)	960 (1760)	93	7.8	6.9	30	108 (3.8)
7	4.7 (1.25)	4.35 (1.15)	22.7 (6.0)	16.20 (4.28)	4,470 (9.85)	700 (1300)	1040 (1900)	143	3.6	3.3	30	204 (7.2)
8	13.3 (3.5)	11.39 (3.01)	22.7 (6.0)	15.90 (4.20)	3,290 (7.25)	940 (1720)	1050 (1920)	160	1.6	1.3	30	360 (12.7)
9	11.4 (3.0)	8.97 (2.37)	9.5 (2.5)	6.55 (1.73)	1,480 (3.26)	1040 (1900)	1080 (1980)	52	2.7	2.8	30	195 (6.9)

---

[a] Volume per hour of the diluted formulation.

[b] Actual atrazine content in the incinerator feed.

[c] The flame temperature was observed at a point approximately 15 cm (6 in.) in from the front wall of the incinerator (see Figure B-1).

[d] Calculated according to Method 3 of "Standards of Performance for New Stationary Sources," *Federal Register*, 36:24876-24895, 23 December 1971.

[e] Retention time is defined as $\frac{V}{v}$, where v is the wet off-gas flow rate from the incinerator at the respective chamber temperature and pressure, and V is the volume of that chamber.

[f] As dry gas at one atmosphere pressure, and 21.1°C (70°F).

Table 69. INCINERATION EFFICIENCY--40.8% ATRAZINE FLOWABLE CONCENTRATE EXPERIMENTS

Run No.	Atrazine feed rate[a] g/hr	Atrazine content of the off-gas[b] g/hr	Ratio of atrazine in off-gas to atrazine fed	Total species[c] content of the off-gas g/hr	Ratio of total species[c] content of off-gas to atrazine fed	Incineration efficiency[d] % Atrazine	Incineration efficiency[d] % Total species[b]
1	1,470	$< 1.6 \times 10^{-2}$	$< 1.1 \times 10^{-5}$	$< 3.8 \times 10^{-2}$	$< 2.6 \times 10^{-5}$	> 99.99	> 99.99
2	1,470	$< 1.6 \times 10^{-2}$	$< 1.1 \times 10^{-5}$	$< 3.1 \times 10^{-2}$	$< 2.1 \times 10^{-5}$	> 99.99	> 99.99
3	1,320	$< 1.1 \times 10^{-2}$	$< 8 \times 10^{-6}$	$< 5 \times 10^{-2}$	$< 4 \times 10^{-5}$	> 99.99	> 99.99
4	1,600	$< 9 \times 10^{-3}$	$< 6 \times 10^{-6}$	$< 5 \times 10^{-2}$	$< 3 \times 10^{-5}$	> 99.99	> 99.99
5	3,420	$< 3.1 \times 10^{-2}$	$< 9 \times 10^{-6}$	$< 1.8 \times 10^{-1}$	$< 5 \times 10^{-5}$	> 99.99	> 99.99
6	3,410	$< 2 \times 10^{-1}$	$< 5 \times 10^{-5}$	$< 2 \times 10^{-1}$	$< 7 \times 10^{-5}$	> 99.99	> 99.98
7	4,470	$< 1.3 \times 10^{-2}$	$< 2.9 \times 10^{-6}$	$< 2.5 \times 10^{-2}$	$< 6 \times 10^{-6}$	> 99.99	> 99.99
8	3,290	$< 2.9 \times 10^{-2}$	$< 9 \times 10^{-6}$	$< 8 \times 10^{-2}$	$< 2.5 \times 10^{-5}$	> 99.99	> 99.99
9	1,480	$< 1.2 \times 10^{-2}$	$< 8 \times 10^{-6}$	$< 2.4 \times 10^{-2}$	$< 1.6 \times 10^{-5}$	> 99.99	> 99.99

---

[a] Actual atrazine content of the incinerator feed.

[b] Atrazine was not detected in all major elements (e.g., impingers) of the gas sampling train. The values given, therefore, include the lower detectable limit for atrazine in these elements.

[c] Atrazine plus all other nitrogenous organic species detected.

[d] Efficiency is defined as: $\left[1 - \frac{\text{quantity } \underline{\text{out}}}{\text{quantity } \underline{\text{in}}}\right] \times 100$, where quantity out is evaluated at Sample Point No. ② (incinerator off-gas), and amount in is evaluated at Sample Point No. ① (the incinerator feed). Efficiencies have been calculated based on (a) atrazine only, and (b) the total nirrogenous organic species detected.

Table 70. OFF-GAS COMPOSITION--40.8% ATRAZINE FLOWABLE CONCENTRATE INCINERATION[a]

Run No.	Atrazine[b] mg/m³	Total species[c] mg/m³	CN^- mg/m³	SO_2 mg/m³	NO_x[e] mg/m³	Total hydrocarbons analyzer: Total hydrocarbons ppm	Total hydrocarbons analyzer: CO ppm	Total hydrocarbons analyzer: CH_4 ppm	Orsat analyzer: O_2 vol. %	Orsat analyzer: CO_2 vol. %	Orsat analyzer: CO vol. %	Moisture vol. %
1	$< 7.7 \times 10^{-2}$	$< 1.8 \times 10^{-1}$	NA[d]	155	306	60	ND[f]	< 1	9.6	8.3	0.0	12.0
2	$< 5.9 \times 10^{-2}$	$< 1.2 \times 10^{-1}$	< 1	122	312	26	ND[f]	< 1	11.8	6.8	0.0	4.6
3	$< 6.1 \times 10^{-2}$	$< 2.6 \times 10^{-1}$	198	106	7	132	348	3	12.4	6.2	0.0	8.7
4	$< 6.4 \times 10^{-2}$	$< 3.5 \times 10^{-1}$	264	144	29	54	223	25	10.2	7.8	0.0	8.3
5	$< 1.1 \times 10^{-1}$	$< 6.6 \times 10^{-1}$	< 1	200	171	42	591	22	9.4	8.4	0.0	11.7
6	< 1.5	< 2.1	5,740	190	126	350	972	177	10.8	6.7	0.7	13.3
7	$< 6.4 \times 10^{-2}$	$< 1.2 \times 10^{-1}$	635	77	76	57	> 7,700[g]	19	12.6	6.0	0.0	9.4
8	$< 8.1 \times 10^{-2}$	$< 2.3 \times 10^{-1}$	< 1	308	278	47	102	32	12.5	6.2	0.0	7.6
9	$< 6.2 \times 10^{-2}$	$< 1.2 \times 10^{-1}$	81	219	64	41	> 7,670	22	7.6	9.6	0.1	8.1

---

[a] As dry gas at one atmosphere pressure, and 21.1°C (70°F).

[b] Atrazine was not detected in all major elements (e.g., impingers) of the gas sampling train. The values given, therefore, include the lower detectable limit for atrazine in these elements.

[c] Atrazine plus all other nitrogenous organic species detected.

[d] No analysis.

[e] Calculated as NO_2.

[f] Not detected.

[g] Upper detection limit.

Table 71. OPERATIONAL DATA SUMMARY--40.8% ATRAZINE FLOWABLE CONCENTRATE EXPERIMENTS

Run No.	1	2	3	4	5	6	7	8	9
Temperature °C (°F)									
Primary chamber (Thermocouple No. ①)	950 (1750)	940 (1730)	670 (1230)	650 (1200)	900 (1660)	520 (970)	650 (1200)	890 (1630)	1020 (1860)
Primary chamber (Thermocouple No. ②)	900 (1650)	920 (1690)	560 (1050)	540 (1010)	850 (1560)	400 (760)	540 (1000)	750 (1380)	1030 (1880)
Primary chamber (Thermocouple No. ③)	1020 (1860)	1020 (1860)	730 (1340)	700 (1290)	940 (1730)	550 (1030)	700 (1300)	940 (1730)	1040 (1900)
Second chamber (Thermocouple No. ④)	850 (1570)	890 (1630)	650 (1200)	620 (1150)	850 (1570)	520 (970)	640 (1180)	900 (1650)	880 (1610)
Second chamber (Thermocouple No. ⑤)	630 (1160)	680 (1260)	480 (900)	440 (820)	680 (1250)	360 (680)	450 (850)	730 (1350)	560 (1040)
Sample Point No. ② (Thermocouple No. ⑥)	350 (660)	390 (740)	260 (500)	210 (410)	390 (740)	190 (370)	260 (500)	500 (940)	330 (630)
Pressures									
Draft (Manometer No. △1), pascals (in H_2O) gauge	32 (0.130)	45 (0.180)	22 (0.090)	19 (0.075)	34 (0.135)	15 (0.060)	44 (0.175)	61 (0.245)	39 (0.155)
Burner operation pressure, pascals (psi) gauge	9.1×10^5 (132)	9.1×10^5 (132)	7.4×10^5 (107)	7.2×10^5 (105)	7.4×10^5 (107)	7.3×10^5 (106)	7.4×10^5 (108)	9.1×10^5 (132)	7.4×10^5 (107)
Scrubber liquids[a]									
1st Stage, H_2O scrubber									
Volume, ℓ (gal.)	1070 (284)	1030 (273)	1090 (288)	1040 (275)	930 (252)	1060 (280)	1060 (279)	1160 (307)	1090 (288)
Atrazine conc., mg/ℓ	$< 5 \times 10^{-3}$ [b]	$< 5 \times 10^{-3}$ [b]	$< 5 \times 10^{-3}$ [b]	1×10^{-2}	$< 5 \times 10^{-3}$ [b]	$< 5 \times 10^{-3}$ [b]	$< 5 \times 10^{-3}$ [b]	$< 5 \times 10^{-3}$ [b]	$< 5 \times 10^{-3}$ [b]
Total species conc.,[c] mg/ℓ	$< 9 \times 10^{-2}$	$< 5 \times 10^{-2}$	$< 2 \times 10^{-2}$	4×10^{-2}	$< 7 \times 10^{-2}$	$< 1 \times 10^{-2}$	4×10^{-2}	$< 8 \times 10^{-2}$	1×10^{-1}
2nd Stage, hexylene glycol scrubber									
Volume, ℓ (gal.)	100 (26.4)	105 (27.8)	104 (27.4)	101 (26.8)	103 (27.1)	103 (27.1)	104 (27.4)	109 (28.9)	106 (28.1)
Atrazine conc.,[b] mg/ℓ	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$
Total species conc., change,[c] mg/ℓ	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$	$< 5 \times 10^{-3}$
3rd Stage, H_2O scrubber									
Volume, ℓ (gal.)	1710 (451)	1690 (446)	1790 (474)	1670 (440)	1840 (486)	1750 (463)	1780 (469)	1820 (480)	1710 (451)
Atrazine conc., mg/ℓ	3×10^{-2}	6×10^{-3}	7×10^{-3}	$< 5 \times 10^{-3}$ [b]	1×10^{-2}	$< 5 \times 10^{-3}$ [b]	$< 5 \times 10^{-3}$ [b]	3×10^{-2}	$< 5 \times 10^{-3}$ [b]
Total species conc.,[c] mg/ℓ	4×10^{-2}	3×10^{-2}	2×10^{-2}	7×10^{-2}	4×10^{-2}	8×10^{-2}	5×10^{-2}	1×10^{-1}	5×10^{-2}
Scrubber system									
Effluent gas (Sample Point No. ⑨)[d]									
Atrazine conc., mg/m³	7×10^{-2}	$< 2 \times 10^{-2}$ [b]	$< 2 \times 10^{-2}$ [b]	$< 2 \times 10^{-2}$ [b]	$< 2 \times 10^{-2}$ [b]	$< 2 \times 10^{-2}$ [b]	$< 2 \times 10^{-2}$ [b]	$< 2 \times 10^{-2}$ [b]	$< 2 \times 10^{-2}$ [b]

---

[a] Scrubber water (Scrubbers 1 and 3) was used once through, while the hexylene glycol (Scrubber 2) was recycled. The concentrations reported for hexylene glycol, therefore, are the concentration changes (increases) detected during the respective tests.

[b] Atrazine was not detected. The values given represent the lower detection limit for atrazine in the respective sample.

[c] Atrazine plus all other nitrogenous organic species detected.

[d] As the wet gas at one atmosphere pressure, and 21.1°C (70°F).

Table 72. SUMMARY OF 80% ATRAZINE WETTABLE POWDER EXPERIMENTS

Run No.	No. 2 fuel oil rate: Nominal burner size ℓ/hr (gal/hr)	No. 2 fuel oil rate: Actual rate ℓ/hr (gal/hr)	Pesticide feed rate: ~ 80% Atrazine formulation kg/hr (lb/hr)	Pesticide feed rate: Contained atrazine[a] g/hr (lb/hr)	Primary chamber temperature °C (°F)	Flame temperature[b] °C (°F)	Excess air[c] %	Retention time sec[d]: Primary chamber	Retention time sec[d]: Second chamber	Sampling time min	Off-gas flow rate[e] m^3/hr (1,000's of SCFH)
A	9.5 (2.5)	8.33 (2.20)	3.63 (8.0)	2,630 (5.8)	1070 (1960)	1050 (1920)	43	2.7	2.8	60	252 (8.9)
B	11.4 (3.0)	8.52 (2.25)	4.45 (9.8)	3,080 (6.8)	970 (1770)	1080 (1970)	125	2.2	3.9	60	346 (12.2)
C	2.8 (0.75)	2.69 (0.71)	3.40 (7.5)	2,130 (4.7)	600 (1120)	940 (1720)	146	5.6	5.2	60	190 (6.7)
D	7.6 (2.0)	6.89 (1.82)	4.26 (9.4)	2,590 (5.7)	970 (1780)	1070 (1950)	71	2.7	3.8	60	269 (9.5)
E	2.8 (0.75)	2.54 (0.67)	4.67 (10.3)	3,220 (7.1)	650 (1200)	980 (1800)	111	6.8	6.4	60	147 (5.2)

---

a/ Actual atrazine content of the ~ 80% atrazine wettable powder formulation.

b/ The flame temperature was observed at a point ~ 15 cm (6 in.) in from the front wall of the incinerator (see Figure B-1).

c/ Calculated according to Method 3 of "Standards of Performance for New Stationary Sources," Federal Register, 36(247):24876-24895, 23 December 1971.

d/ Retention time is defined as $\frac{V}{v}$, where v is the wet off-gas flow rate from the incinerator at the respective chamber temperature and pressure, and V is the volume of that chamber.

e/ As dry gas at one atmosphere pressure, and 21.1°C (70°F).

Table 73. RESIDUE AND OFF-GAS CHARACTERISTICS--80% ATRAZINE WETTABLE POWDER INCINERATION

	Pesticide feed rate		Solid residue						
			Primary chamber			Second chamber			
Run No.	~ 80% Atrazine formulation kg/hr (lb/hr)	Contained atrazine[a] g/hr	Total g/hr	Atrazine conc. ppm	Total species[b] conc. ppm	Total g/hr	Atrazine conc. ppm	Total species[b] conc. ppm	Ratio of total incinerator residue to total charge
A	3.63 (8.0)	2,630	54	10.4	10.4	101	8.4	8.4	0.042
B	4.45 (9.8)	3,080	79	18.9	20.8	23	6.5	6.5	0.023
C	3.40 (7.5)	2,130	58	14.0	15.2	61	2.4	4.6	0.035
D	4.26 (9.4)	2,590	75	2.3	2.3	23	6.2	9.0	0.023
E	4.67 (10.3)	3,220	123	14.0	14.0	29	5.2	5.2	0.032

Run No.	Atrazine content of off-gas g/hr	Atrazine content of solid residue g/hr	Atrazine content of off-gas and solid residue g/hr	Total species content[b] of off-gas g/hr	Total species[b] content of solid residues g/hr	Total species[b] content of off-gas and solid residues g/hr	Ratio of atrazine in off-gas to to total atrazine fed	Ratio of total species[b] in off-gas to total atrazine fed	Incineration efficiency[c]	
									Atrazine	Total species[b]
A	1.2×10^{-3}	1.2×10^{-3}	2.4×10^{-3}	1.4×10^{-3}	1.2×10^{-3}	2.6×10^{-3}	4.6×10^{-7}	5×10^{-7}	> 99.99	> 99.99
B	$6 \times 10^{-}$[illegible]	1.6×10^{-3}	2.[illegible] $\times 10^{-3}$	2.0×10^{-3}	1.8×10^{-3}	3.8×10^{-3}	1.8×10^{-7}	6×10^{-7}	> 99.99	> 99.99
C	5×10^{-4}	1×10^{-3}	1.5×10^{-3}	2.3×10^{-3}	1.2×10^{-3}	3.5×10^{-3}	2.5×10^{-7}	1.1×10^{-6}	> 99.99	> 99.99
D	8×10^{-4}	3.2×10^{-4}	1.1×10^{-3}	2.2×10^{-3}	3.8×10^{-4}	2.6×10^{-3}	3.0×10^{-7}	8×10^{-7}	> 99.99	> 99.99
E	1×10^{-4}	2×10^{-3}	2×10^{-3}	1×10^{-3}	2×10^{-3}	3×10^{-3}	3×10^{-8}	3×10^{-7}	> 99.99	> 99.99

---

a/ Actual atrazine content of the ~ 80% wettable powder formulation.

b/ Atrazine plus all other nitrogenous organic species detected.

c/ Efficiency is defined as $\left[1 - \frac{\text{quantity out}}{\text{quantity in}}\right] \times 100$, where the quantity out is evaluated at Sample Points Nos. ② (incinerator off-gas) and ③ (incinerator residues) and the quantity in is evaluated at Sample Point No. ① (the incinerator feed). Efficiencies have been calculated based on (a) atrazine only, and (b) the total nitrogenous organic species detected at Sample Points Nos. ② and ③.

Table 74. OFF-GAS COMPOSITION--80% ATRAZINE WETTABLE POWDER INCINERATION[a]

						Total hydrocarbons analyzer			Orsat analyzer			
Run No.	Atrazine mg/m^3	Total species[b] mg/m^3	CN^- mg/m^3	SO_2 mg/m^3	NO_x[c] mg/m^3	Total hydrocarbons ppm	CO ppm	CH_4 ppm	O_2 vol. %	CO_2 vol. %	CO vol. %	Moisture vol. %
A	4.8×10^{-3}	5.6×10^{-3}	38	491	218	38	> 7,970[d]	35	6.6	10.4	0.0	11.6
B	1.6×10^{-3}	5.8×10^{-3}	< 1	241	333	26	441	26	12.0	6.7	0.0	7.2
C	2.8×10^{-3}	1.2×10^{-2}	919	332	77	37	127	53	12.7	6.3	0.0	5.3
D	2.9×10^{-3}	8.2×10^{-3}	1	304	517	20	357	26	9.1	8.7	0.0	7.9
E	6.8×10^{-4}	7.5×10^{-3}	316	455	86	55	160	83	11.4	6.9	0.0	5.0

---

[a] As dry gas at one atmosphere pressure, and 21.1°C (70°F).
[b] Atrazine plus all other nitrogenous organic species detected.
[c] Calculated as NO_2.
[d] Upper detection limit.

Table 75. PARTICULATE SAMPLING SUMMARY--80% ATRAZINE WETTABLE POWDER EXPERIMENTS

Description	A	B	C	D	E
Vol. dry gas - std. cond., nm^3	0.440	0.589	0.334	0.465	0.254
Percent moisture by vol.	8.6	6.2	9.5	8.5	9.6
Avg. stack temperature, °C	280.8	372.0	173.9	297.5	210.0
Stk. flow rate, dry., std. cn., nm^3/min	4.2	5.7	3.2	4.5	2.4
Actual stack flow rate, m^3/min	8.6	13.3	5.3	9.4	4.4
Percent isokinetic	99.6	98.2	100.4	99.4	100.4
Percent excess air	43	124	143	72	112
Particulates - partial catch					
Particulate wt. - partial, mg	763	704	762	968	993
Part. load - ptl., std. cn., mg/nm^3	1,730	1,190	2,280	2,080	3,800
Part. load - ptl., stk. cn., mg/m^3	852	513	1,360	988	2,170
Partic. emis. - partial, kg/hr	0.439	0.410	0.435	0.558	0.567
Particulates - total catch					
Particulate wt. - total, mg	790	577	820	1,280	1,100
Part. load - ttl., std. cn., mg/nm^3	1,790	977	2,450	2,750	4,330
Part. load - ttl., std. cn., corrected to 12% CO_2, mg/nm^3	2,060	1,750	4,700	3,790	7,500
Part. load - ttl., stk. cn., mg/m^3	883	420	1,470	1,310	2,400
Partic. emis. - total, kg/hr	0.454	0.336	0.468	0.739	0.629
Percent impinger catch	3.42	22.04	7.13	24.53	9.92

Table 76. OPERATIONAL DATA SUMMARY--80% ATRAZINE WETTABLE POWDER EXPERIMENTS

Description	A	B	C	D	E
Vol. dry gas - std. cond., nm^3	0.440	0.589	0.334	0.465	0.254
Percent moisture by vol.	8.6	6.2	9.5	8.5	9.6
Avg. stack temperature, °C	280.8	372.0	173.9	297.5	210.0
Stk. flow rate, dry., std. cn., nm^3/min	4.2	5.7	3.2	4.5	2.4
Actual stack flow rate, m^3/min	8.6	13.3	5.3	9.4	4.4
Percent isokinetic	99.6	98.2	100.4	99.4	100.4
Percent excess air	43	124	143	72	112
Particulates - partial catch					
Particulate wt. - partial, mg	762.60	703.80	761.70	968.00	993.00
Part. load - ptl., std. cn., mg/nm^3	1,727.67	1,192.60	2,277.26	2,075.87	3,897.91
Part. load - ptl., stk. cn., mg/m^3	852.49	512.94	1,363.32	987.51	2,165.02
Partic. emis. - partial, kg/hr	0.439	0.410	0.435	0.558	0.567
Particulates - total catch					
Particulate wt. - total, mg	789.60	576.70	820.20	1,282.70	1,102.30
Part. load - ttl., std. cn., mg/nm^3	1,788.84	977.23	2,452.15	2,750.74	4,326.96
Part. load - ttl., stk. cn., mg/m^3	882.67	420.31	1,468.03	1,308.56	2,403.32
Partic. emis. - total, kg/hr	0.454	0.336	0.468	0.739	0.629
Percent impinger catch	3.42	22.04	7.13	24.53	9.92

Liquid formulation Run no.	Primary chamber temperature °C (°F)	Excess air (%)	Cyanide content[a/] mg/m^3	Cyanide content[a/] g/hr
1	1020 (1860)	79	NA[b/]	NA
2	1020 (1860)	123	< 1	< 0.3
3	730 (1340)	138	198	36
4	700 (1290)	90	264	38
5	970 (1780)	76	< 1	< 0.3
6	550 (1030)	93	5,740	620
7	700 (1300)	143	635	130
8	940 (1720)	140	< 1	< 0.4
9	1040 (1900)	52	81	16
Dust formulation Run no.				
A	1070 (1960)	43	38	10
B	970 (1770)	125	< 1	< 0.3
C	600 (1120)	146	919	175
D	970 (1780)	71	1	0.3
E	650 (1200)	111	316	46

[a/] Calculated as CN^-.

[b/] No analysis.

Incineration of atrazine at the lower temperature, ~ 650°C (1200°F), yielded high levels of cyanide in the effluent, i.e., 198 to 5,738 mg/m^3. The higher temperatures, ~ 1000°C (1830°F), generally yielded much lower concentrations. However, only those tests conducted at the higher temperature and relatively high excess air rates (> 75%) routinely yield concentrations of < 1 mg/m^3. . Thus, it appears that temperatures of about 1000°C (1830°F) and excess air of > 75% are required to incinerate atrazine and obtain cyanide concentration in the undiluted effluent of < 1 mg/m^3.

The results from particulate sampling are shown in Table 75. All runs were within acceptable isokinetic limits (100 ± 10%). The wettable powder formulation of atrazine followed the previous trend, although not as high, of particulate emission levels which exceed established limits. The incineration of atrazine wettable powder formulations will therefore require a particulate emissions control system.

DISCUSSION

The only operational problem encountered with atrazine incineration was the plugging of the liquid formulation injection nozzle. Insulation of this nozzle with the water-jacketed dust nozzle, as discussed above, overcame this problem.

It should be noted that the high concentration of active ingredients in the dust formulation (80%) made the desired active ingredient injection rate more difficult to attain.

References

1. Lawless, E. W., T. L. Ferguson, and A. F. Meiners, "Guidelines for the Disposal of Small Quantities of Unused Pesticides," (Draft), EPA Contract No. 68-01-0098 (1974).

2. Putnam, R. C., F. Ellison, R. Protzmann, and J. Hilovsky, "Organic Pesticides and Pesticide Containers--A Study of Their Decontamination and Combustion," Foster D. Small, Inc., Final Report on Contract No. CPE 69-140 (1971).

3. von Rümker, R., E. W. Lawless, and A. F. Meiners, "Production, Distribution, Use and Environmental Impact Potential of Selected Pesticides," Contract No. EQC-311 (1974).

4. Kennedy, M. V., B. J. Stojanovic, and F. L. Shuman, Jr., "Chemical and Thermal Methods for Disposal of Pesticides," Res. Rev., 29:89 (1969).

VII. CAPTAN

PESTICIDE DESCRIPTION

Physical Properties

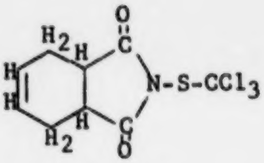
Chemical Name: N-(trichloromethylthio)-4-cyclohexene-1,2-dicarboximide

Common Name: Captan

Trade Names: Merpan®, Orthocide®, SR-406, Vanicide

Pesticide Class: Fungicide; chlorinated organosulfur compound

Structural Formula:



Empirical Formula: $C_9H_8Cl_3NO_2S$

Molecular Weight: 300.61

Analysis: C, 35.96%; H, 2.69%; N, 4.67; Cl, 35.50%; S, 10.67%; O, 10.65%

Physical State:	Pure	Technical
	White crystals	Yellow to buff-colored amorphous powder
Odor:	Odorless	Pungent
Melting Point:	178°C (Martin)[1] 174 to 176°C (Stauffer)[2] 172 to 173°C (Merck)[3]	160 to 170°C (Martin) 158 to 164°C (Stauffer)
Boiling Point:	Decomposes near melting point	
Specific Gravity (20/20°C):	1.73	1.62

	Pure	Technical
Bulk Density:		25 to 30 lb/ft^3

Vapor Pressure: 6 x 10^{-5} mm Hg at 25°C

pH: Typically 8.0 to 8.3

Particle Size: 9 to 13 μ surface average diameter by air permeation

Captan Content in Technical Product (Stauffer)[2/]: 92% Typical, seldom less than 90% or more than 94%.

Noncaptan Chlorine (Stauffer)[2/]: Analysis by chlorine content typically gives results almost 2% too high when calculated as captan.

Solubility of Captan in Various Solvents (Stauffer)[2/]:

Substance	Grams/100 ml of solvent (25°C)
Tetrachloroethane	8.15
Chloroform	8.0
Xylene	6.5
Dioxolane	5.0
Cyclohexanone	4.96
Dioxane	4.7
Ethyl acetate	4.5
Benzonitrile	4.0 (12°C)
Acetonitrile	3.6 (12°C)
Chlorobenzene	3.3
Methyl chloride	3.0
Acetone	3.0
Ethylene chloride	2.85
Nitromethane	2.0
Velsicol AR-50	Less than 2
Benzene	1.8
Isopropyl alcohol	0.8
Toluene	0.7
Methyl alcohol	0.5
Ethanol	0.29
Diethyl ether	0.25
Heptane	0.04
Stove oil	
Carbitol	
Water	Less than 0.5 ppm 3.3 ppm (Chevron)[4/]

Chemical Properties

The chemistry of captan reported in the literature primarily concerns degradation reactions. Captan is reported to be decomposed by hydrolysis (essentially complete hydrolysis of a 2% slurry at 100°C in 2-1/2 hr); thermal decomposition; and photolysis.

von Rümker and Horay[5] state that dry captan is stable to heat but aqueous suspensions are quickly decomposed at 100°C or in alkaline media. The following thermal stabilities for dry captan are given:

Half-life at 80°C	213 weeks
Half-life at 120°C	14-1/4 days

At temperatures above the melting point dry captan is reported to be rapidly decomposed (Melnikov).[6]

Pyrolysis of captan by dry distillation at 200°C is reported to result in the formation of thiophosgene, tetrahydrophthalimide and "other related products" (California Spray-Chemical Corporation[7]).

Production and Use

Captan is a contact fungicide that is effective against a fairly broad spectrum of plant-pathogenic fungi. It is registered and recommended in the United States for use on more than 70 different crops (EPA).[8]

An estimated 16 million pounds of captan were used in the United States in 1972--about 10 million pounds in agricuilture and 6 million by home gardeners (Midwest Research Institute).[9]

Captan is domestically available in a great variety of dry formulations, i.e., wettable powders and dusts of various concentrations. Because of its physical and chemical properties, captan active ingredient cannot readily be dissolved or formulated into liquids. No emulsifiable captan formulations are currently available.

FORMULATIONS TESTED

Because captan is available only in solid forms, only one formulation was tested--a 50% wettable powder.

Name: Ortho Orthocide® 50 Wettable

Manufacturer: Chevron Chemical Company, Ortho Division, San Francisco, California

Composition: Active ingredient (by weight)

Captan*	50%
Inert ingredients	50%

---

* N-(trichloromethylthio)-4-cyclohexene-1,2-dicarboximide.

Registration: EPA Reg. No. 239-533

Lot No.: M30943 CK 90

Particle Size Specifications: Formulated from 544 parts by weight technical material (92% captan) 424 parts clay, and 32 parts other inert material such that > 99.9% passes a 44 μ (325 mesh) sieve with brushing.

PRELIMINARY THERMAL ANALYSIS

Laboratory thermal analysis of the powder as well as technical captan gave the following results:

Sample	Test	Test method	Result
Technical captan	Sulfur	ASTM D-129	11.69%
	Calorific value	ASTM D-2015	1.619×10^{7} J/kg (6,966 Btu/lb)
Captan wettable powder (50%)	Sulfur	ASTM D-129	6.84%
	Calorific value	ASTM D-2015	9.166×10^{6} J/kg (3,944 Btu/lb)

Figures 53 and 54 show the results of DTA and TGA of the technical grade captan. DTA data show a distinct endotherm at about 185°C which approximately corresponds to the reported melting point of pure captan (m.p. range 172 to 178°C). In addition, the data show two distinct exotherms at about 250 and 550°C indicating decomposition of the compound. The decomposition process is substantiated by the TGA data which indicate that about 75% of the compound is lost at about 250°C, and almost all of the compound is lost at 600°C.

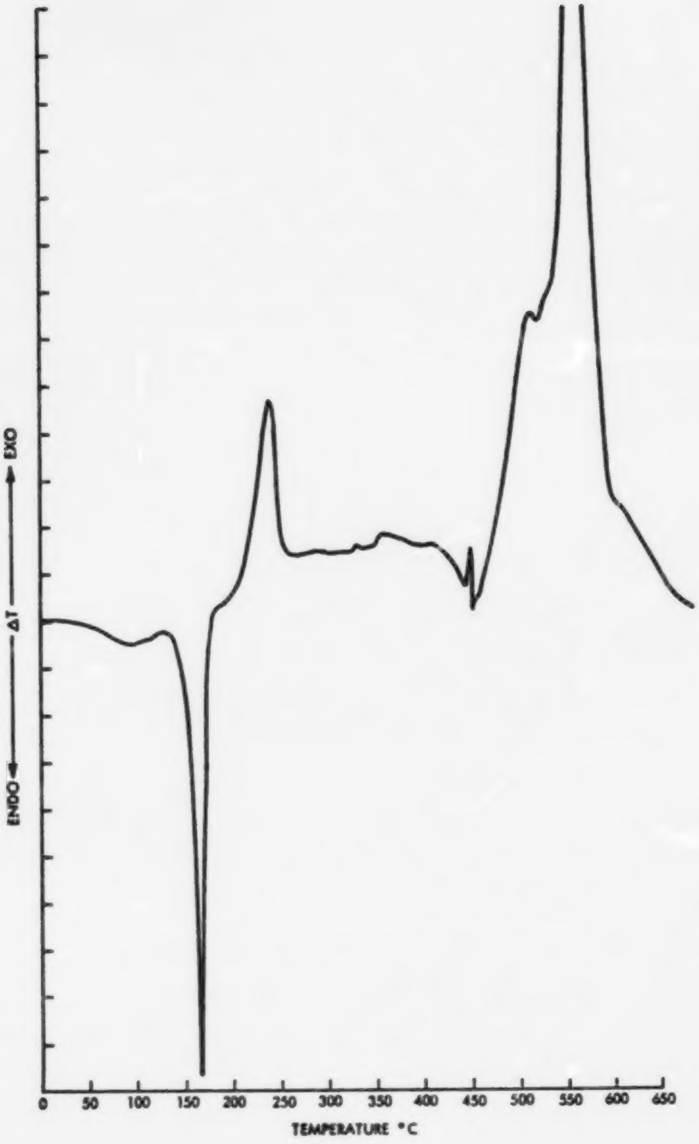
Figures 55 and 56 show the results of DTA and TGA data on a 50% captan wettable powder formulation. DTA data of this powder formulation show a similar pattern of endotherm and exotherms as that of the technical grade, i.e., an endotherm at about 185°C (indicating possible melting), and two exotherms at about 220 and 530°C, respectively (indicating decomposition). Again, the decomposition process is substantiated by the TGA data which indicate approximately 50% lost in sample weight at 250°C and 60% less at the completion of the experiment (at 1000°C). The weight loss due to decomposition corresponds (within experimental error) to the amount of captan (50%), in the formulation.

METHODS OF ANALYSIS

Apparatus

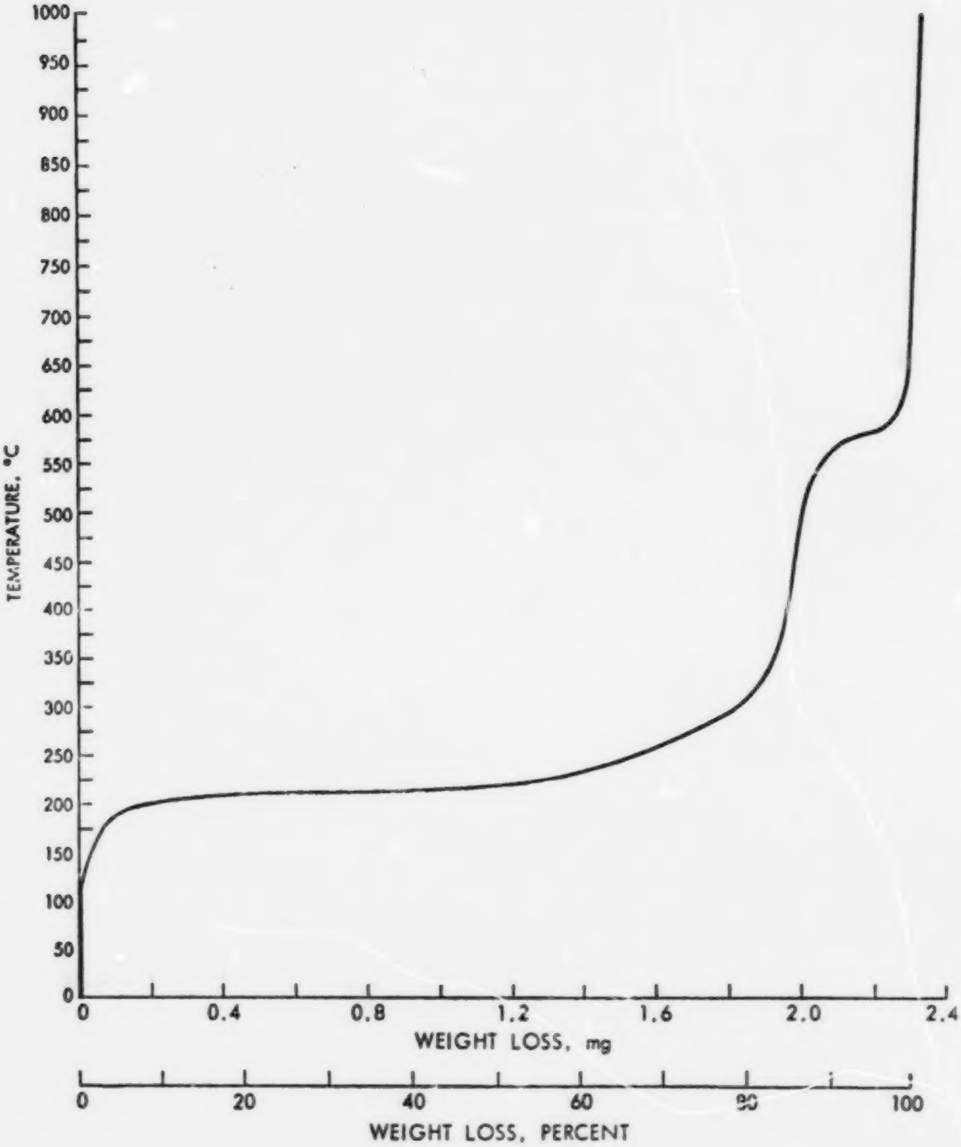
Two instruments were used for captan analysis. One, a Micro-Tek 2000R gas chromatograph equipped with an 18-in., 4 mm I.D. glass column (packed with 1.5% OV-17 + 1.95% QF-1 on 100/120 mesh Supelcoport from Supelco, Inc., Bellefonte, Pennsylvania), and a tritium electron capture detector, maintained at a voltage of 10 V DC was used for gas chromatographic analysis of all impinger samples collected at Sample Point No. ② of the incinerator. Chromatographic operating conditions were: injector temperature, 155°C; column temperature, 150°C; detector temperature, 180°C; carrier flow rate, 125 ml/min, N_2; and purge gas flow rate, 275 ml/min, N_2.

A Hewlett-Packard 3380A integrator was utilized for peak identification and quantification.



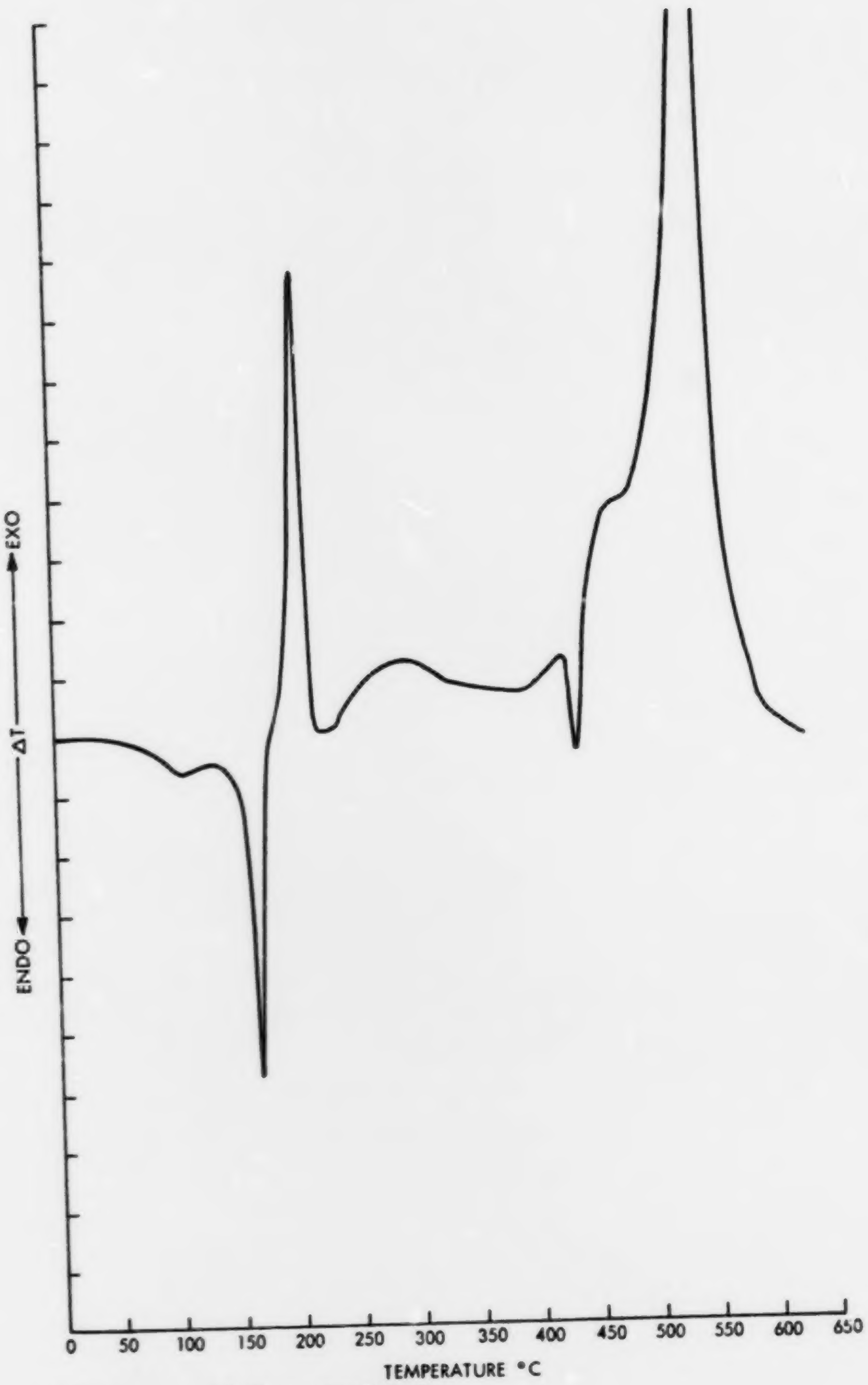
Reference: Al_2O_3 + Kaolinite
Prog. mode: Heat
Rate: 20°C/min
Start: 25°C

Figure 53. DTA of technical captan



Sample weight: 2.340 mg
Heating rate: 20°C/min
Environment: ~ 20 ml/min air (20% O_2, 80% N_2)

Figure 54. TGA of technical captan.

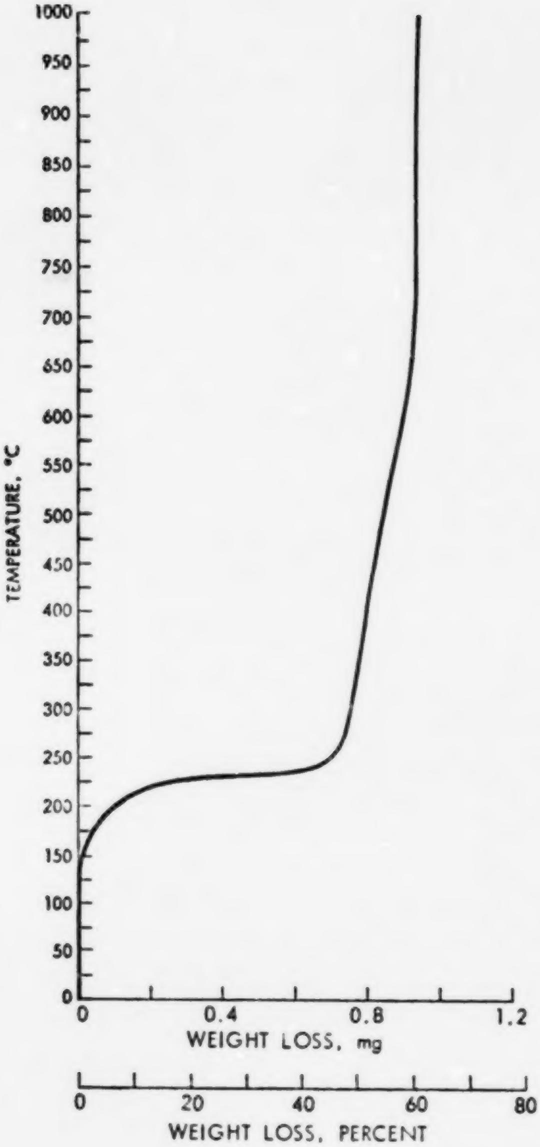


Reference: Al_2O_3 + Kaolinite

Prog. mode: Heat

Rate: 20°C/min

Figure 55. DTA of a 50% captan wettable powder



Sampling weight: 1.568 mg
Heating rate: 20°C/min
Environment: ~ 20 ml/min air (20% O_2, 80% N_2)

Figure 56. TGA of 50% captan wettable powder

The other instrument used was a Varian 1400 gas chromatograph equipped with an Aerograph Scandium Tritide electron capture detector (polarizing voltage: -90 V DC) and a 6-ft, 4 mm I.D. glass column (packed with 1.5% OV-17 + 1.9% QF-1 on 100/120 mesh Supelcoport from Supelco, Inc.). This instrument was used for the analysis of all samples other than those collected at Sample Point No. ② . Chromatographic operating conditions were: injector temperature, 180°C; column temperature, 190°C; detector temperature, 200°C; carrier flow rate, 35 ml/min, N_2; and no purge flow (as per manufacturer's recommendations).

A Heath-Schlumberger Model SR-255B strip chart recorder was used to record the chromatograms.

Reagents and Materials

Two standard materials, captan (98.6% pure) and aldrin (97% pure) were used. Solvents used were pesticide grade benzene (Fisher Scientific) for all impingers and standard captan samples, pesticide grade 2,2,4-trimethylpentane (Mallinckrodt) for standard aldrin solutions and pesticide grade hexane (Matheson, Coleman, Bell) for extraction of hexylene glycol traps from the second stage scrubber. All laboratory glassware (vials, beakers, pipettes, etc.) was washed in Alconox detergent (Scientific Products) and rinsed with deionized distilled water and reagent grade acetone (Fisher Scientific).

Standards and Calibration Curves

The solid standards, captan and aldrin, provided by USEPA, were used to prepare stock standard solutions of 100 g/ml each. On the Micro-Tek 2000R, separate captan and aldrin calibration curves were obtained by dilutions of various amounts of stock solutions (captan range used: 0.0 to 2.0 ng; aldrin range used: 0.0 to 200 pg). On the Varian 1400 the aldrin and captan standards were combined and linear calibration curves were obtained from this composite standard (captan range used: 0 to 800 pg; aldrin range used: 0 to 100 pg). In the samples captan peaks were quantified against the captan calibration curve and all other peaks were quantified according to the aldrin curve.

Procedure for Sample Preparation

The mass of collected particulates was determined for all elements of the sample train at Sample Point No. ② as follows. All samples were taken to dryness under a hood in clean, dessicated, tared 250-ml beakers and dessicated 2 days before final weighing. The residue was extracted with benzene (two 10-to 15-ml portions) and the extract taken just to dryness and capped tightly. The silica gel was extracted with a known volume of benzene to cover and a 20-ml portion pipetted into vials and taken just to dryness. All other impinger, wash and blank solutions, were taken just to dryness in the French Square bottles as they were received. Ten milliliters of the hexylene glycol traps from the second stage scrubber were extracted with n-hexane and the extract was taken just to dryness. All samples were taken up in appropriate amounts of benzene just prior to GC analysis.

Portions of all cleanout samples (primary chamber, secondary chamber, etc.) were weighed out and extracted and the extracts were analyzed for captan.

Analysis and Discussion

All samples were analyzed for captan. Unidentified chromatographic peaks were quantitated against the aldrin calibration curve because the response range of captan was not low enough to include many of these unidentified peaks.

The sensitivity of the instrument is 50 pg for captan and 1 pg for aldrin. Based on these sensitivity values, and with a 5-μl sample injection for each analysis, the minimum detectable quantities for a 20-ml sample solution are 0.2 μg for captan and 4 ng for aldrin. However, during the analysis, samples were very often concentrated down to 1 ml, resulting in minimum detectable quantities of 10 ng for captan and 0.2 ng for aldrin.

Major problems were encountered on the Micro-Tek 2000R while running captan. It appeared initially that sensitivity was low; and a new column was packed. It then became apparent that the captan was degrading between the injector and the detector. Resolution of this problem involved working at lower column and inlet temperatures and silanization of all pieces of the chromatograph through which the sample traveled.

TEST CONDITIONS AND RESULTS

Eight tests were made using the 50% captan wettable powder formulation. The results of these tests are summarized in Tables 77 through 81.

As is shown in Table 78, the efficiency of combustion was > 99.99% for all eight tests, whether based on captan or total chlorinated species detected in the off-gas and incinerator residues. No correlation has been found between the relative rate of captan and total chlorinated species in the incinerator off-gas (fourth and third to last columns in Table 78) and specific operating conditions.

Table 77. SUMMARY OF 50% CAPTAN WETTABLE POWDER EXPERIMENTS

	No. 2 fuel oil rate		Pesticide feed rate					Retention time[d/] sec			
Run No.	Nominal burner size ℓ/hr (gal/hr)	Actual rate ℓ/hr (gal/hr)	~ 50% Captan formulation kg/hr (lb/hr)	Contained captan[a/] g/hr (lb/hr)	Primary chamber temperature °C (°F)	Flame temperature[b/] °C (°F)	Excess air[c/] %	Primary chamber	Second chamber	Sampling time min	Off-gas flow rate[e/] m^3/hr (1,000's of SCFH)
A	7.6 (2.0)	8.71 (2.30)	6.44 (14.2)	2,880 (6.35)	1000 (1830)	1160 (2120)	137	1.8	1.8	60	391 (13.8)
B	7.6 (2.0)	5.75 (1.52)	6.49 (14.3)	2,850 (6.28)	920 (1690)	1120 (2040)	94	3.2	3.2	60	241 (8.5)
C	9.5 (2.5)	8.82 (2.33)	3.58 (7.9)	1,640 (3.62)	1010 (1850)	1180 (2160)	76	2.5	2.5	60	278 (9.8)
D	9.5 (2.5)	9.24 (2.44)	3.54 (7.8)	1,110 (2.45)	980 (1790)	1190 (2170)	135	2.0	1.9	60	396 (14.0)
E	3.8 (1.0)	3.56 (0.94)	3.54 (7.8)	1,250 (2.76)	660 (1220)	1120 (2040)	192	4.2	3.9	60	235 (8.3)
F	3.8 (1.0)	3.82 (1.01)	3.49 (7.7)	1,410 (3.11)	670 (1230)	1100 (2010)	130	5.3	5.1	60	187 (6.6)
G	2.8 (0.75)	2.73 (0.72)	6.35 (14.0)	2,230 (4.92)	650 (1200)	1040 (1900)	252	6.8	6.4	60	150 (5.3)
H	3.8 (1.0)	3.71 (0.98)	6.17 (13.6)	2,040 (4.50)	690 (1280)	1080 (1980)	99	6.7	6.5	60	144 (5.1)

[a/] Actual captan content of the ~ 50% captan wettable powder formulation.

[b/] The flame temperature was observed at a point approximately 15 cm (6 in.) in from the front wall of the incinerator (see Figure B-1).

[c/] Calculated according to Method 3 of "Standards of Performance for New Stationary Sources," *Federal Register*, 36(247):24876-24895, 23 December 1971.

[d/] Retention time is defined as $\frac{V}{v}$, where v is the wet off-gas flow rate from the incinerator at the respective chamber temperature and pressure, and V is the volume of that chamber.

[e/] As dry gas at one atmosphere pressure, and 21.1°C (70°F).

Table 78. INCINERATION EFFICIENCY--50% CAPTAN WETTABLE POWDER EXPERIMENTS

Run No.	Pesticide feed rate		Solid residue						Ratio of total incinerator residue to total charge
			Primary chamber			Second chamber			
	~ 50% Captan formulation kg/hr (lb/hr)	Contained captan a/ g/hr (lb/hr)	Total g/hr	Captan conc. ppm	Total species b/ conc., ppm	Total g/hr	Captan conc. ppm	Total species b/ conc., ppm	
A	6.44 (14.2)	2,880 (6.35)	540	0.06	0.14	358	0.20	0.27	0.14
B	6.49 (14.3)	2,850 (6.28)	957	0.11	0.21	205	0.69	0.88	0.18
C	3.58 (7.9)	1,640 (3.62)	301	0.15	0.22	172	0.56	0.74	0.13
D	3.54 (7.8)	1,110 (2.45)	370	0.12	0.16	115	0.28	0.46	0.14
E	3.54 (7.8)	1,250 (2.76)	342	0.01	0.02	146	0.15	0.15	0.14
F	3.49 (7.7)	1,410 (3.11)	353	0.01	0.02	120	0.03	0.13	0.14
G	6.35 (14.0)	2,230 (4.92)	713	0.04	0.07	319	0.06	0.02	0.16
H	6.17 (13.6)	2,040 (4.50)	625	0.73	0.83	453	0.08	1.12	0.18

Run No.	Captan content of off-gas g/hr	Captan content of solid residues g/hr	Captan content of off-gas and solid residues g/hr	Total species b/ content of off-gas g/hr	Total species b/ content of solid residues g/hr	Total species b/ content of off-gas and solid residue g/hr	Ratio of captan in off-gas to total captan fed	Ratio of total species b/ in off-gas to total captan fed	Incineration efficiency e/ %	
									Captan	Total species b/
A	$< 7 \times 10^{-4}$ c/	1.0×10^{-4}	$< 8 \times 10^{-4}$	< 4.[illegible] $\times 10^{-3}$	$< 1.7 \times 10^{-4}$	4.2×10^{-3}	$< 2.6 \times 10^{-7}$	$< 1.4 \times 10^{-6}$	> 99.99	> 99.99
B	$< 1.6 \times 10^{-4}$ c/	2.5×10^{-4}	$< 5 \times 10^{-4}$	< 4 [illegible] $\times 10^{-3}$	$< 3.8 \times 10^{-4}$	5×10^{-3}	$< 9 \times 10^{-8}$	$< 1.7 \times 10^{-6}$	> 99.99	> 99.99
C	$< 1.4 \times 10^{-5}$ c/	1.4×10^{-4}	$< 1.5 \times 10^{-4}$	$< 1.9 \times 10^{-3}$	$< 1.9 \times 10^{-4}$	2.1×10^{-3}	$< 8 \times 10^{-9}$	$< 1.2 \times 10^{-6}$	> 99.99	> 99.99
D	2.5×10^{-5}	8×10^{-5}	1.0×10^{-4}	1.2×10^{-3}	1.1×10^{-4}	1.3×10^{-3}	2.2×10^{-8}	1.1×10^{-6}	> 99.99	> 99.99
E	$< 3.2 \times 10^{-5}$ c/	2.5×10^{-5}	$< 6 \times 10^{-5}$	$< 2.5 \times 10^{-3}$	$< 2.9 \times 10^{-5}$	2.5×10^{-3}	$< 2.6 \times 10^{-8}$	$< 2.0 \times 10^{-6}$	> 99.99	> 99.99
F	$< 2.3 \times 10^{-6}$ c/	7×10^{-6}	$< 9 \times 10^{-6}$	$< 5 \times 10^{-3}$	$< 2.3 \times 10^{-5}$	5×10^{-3}	$< 1.6 \times 10^{-9}$	$< 3.8 \times 10^{-6}$	> 99.99	> 99.99
G	6×10^{-4}	5×10^{-5}	7×10^{-4}	5×10^{-3}	6×10^{-5}	5×10^{-3}	3×10^{-7}	2×10^{-6}	> 99.99	> 99.99
H	$< 1 \times 10^{-5}$ d/	5×10^{-4}	$< 5 \times 10^{-4}$	$< 6 \times 10^{-4}$	$< 1 \times 10^{-3}$	2×10^{-3}	$< 5 \times 10^{-9}$	$< 3 \times 10^{-7}$	> 99.99	> 99.99

---

a/ Captan content of the ~ 50% captan wettable powder formulation.

b/ Captan as well as other chlorinated hydrocarbon species detected.

c/ Captan was not detected in all elements (e.g., impingers) of the gas sampling train. The value given, therefore, includes the lower detectable limit for captan in these elements.

d/ Captan not detected. The value given represents the captan detection limit for the particular sample.

e/ Efficiency is defined as $\left[1 - \frac{\text{quantity out}}{\text{quantity in}}\right] \times 100$, where the quantity out is evaluated at Sample Points Nos. ② (incinerator off-gas) and ③ (incinerator residues), and the quantity in is evaluated at Sample Point No. ① (the incinerator feed). Efficiencies have been calculated based on (a) captan only, and (b) the total chlorinated hydrocarbon species detected at Sample Points Nos. ② and ③.

Table 79. OFF-GAS COMPOSITION--50% CAPTAN WETTABLE POWDER INCINERATION[a]

Run No.	Captan mg/m³	Total species[b] mg/m³	CN⁻ mg/m³	SO_2 mg/m³	NO_x[f] mg/m³	Total hydrocarbons analyzer: Total hydrocarbons ppm	Total hydrocarbons analyzer: CO ppm	Total hydrocarbons analyzer: CH_4 ppm	Orsat analyzer: O_2 vol. %	Orsat analyzer: CO_2 vol. %	Orsat analyzer: CO vol. %	Moisture vol. %
A	$< 1.9 \times 10^{-3}$ [b]	$< 1.0 \times 10^{-2}$	77	2,050	138	18	NA	NA	12.4	6.4	0.0	8.1
B	$< 1.1 \times 10^{-3}$ [b]	$< 2.0 \times 10^{-2}$	129	3,540	165	3	16	2	10.5	8.0	0.0	8.5
C	$< 5.0 \times 10^{-5}$ [b]	$< 6.8 \times 10^{-3}$	46	1,960	336	38	8	< 1	9.4	8.7	0.1	9.2
D	6.0×10^{-5}	2.9×10^{-3}	49	1,550	175	15	10	< 1	12.3	6.5	0.0	4.6
E	$< 1.2 \times 10^{-4}$ [b]	$< 9.8 \times 10^{-3}$	NA[e]	2,090	199	15	399	2	14.0	5.3	0.0	7.6
F	$< 1.1 \times 10^{-5}$ [b]	$< 2.6 \times 10^{-2}$	27	2,970	208	23	217	14	12.2	6.6	0.1	8.4
G	4.0×10^{-3}	2.9×10^{-2}	107	5,780	130	12	1,340	3	15.2	4.4	0.0	7.7
H	$< 6.9 \times 10^{-5}$ [c]	$< 4.0 \times 10^{-3}$	133	5,620	39	7	1,100	2	10.7	8.0	0.1	8.3

---

[a] As dry gas at one atmospheric pressure, and 21.1°C (70°F).

[b] Captan was not detected in all elements (e.g., impingers) of the gas sampling train. The values given, therefore, includes the lower detectable limit for captan in these elements.

[c] Captan not detected. The value given represents the captan detection limit for the particular sample.

[d] Captan plus all other chlorinated hydrocarbon species detected.

[e] No analysis.

[f] Calculated as NO_2.

Table 80. PARTICULATE SAMPLING SUMMARY--50% CAPTAN WETTABLE POWDER EXPERIMENTS

Description	A	B	C	D	E	F	G	H
Vol. dry gas - std., cond., nm^3	0.670	0.419	0.488	0.672	0.405	0.323	0.257	0.251
Percent moisture by vol.	8.1	8.5	9.2	4.6	7.6	8.4	7.7	8.3
Avg. stack temperature, °C	311.8	252.1	328.9	333.6	193.8	171.1	196.1	218.3
Stk. flow rate, dry, std. cond., nm^3/min	6.5	4.0	4.6	6.6	3.9	3.1	2.5	2.4
Actual stack flow rate, m^3/min	13.9	7.8	10.5	14.2	6.8	5.1	4.3	4.4
Percent isokinetic	98.5	100.6	100.3	97.2	98.3	99.2	98.4	99.2
Percent excess air	137	95	77	135	192	132	252	99
Particulates - partial catch								
Particulate wt. - partial, mg	2,760	3,130	1,530	2,140	2,060	2,420	5,600	5,240
Part. load - ptl., std. cn., mg/nm^3	4,110	7,460	3,120	3,180	5,070	7,470	21,800	20,900
Part. load - ptl., stk. cn., mg/m^3	1,920	3,800	1,380	1,480	2,940	4,540	12,600	11,500
Partic. emis. - partial, kg/hr	1.604	1.783	0.872	1.263	1.200	1.394	3.262	3.026
Particulates - total catch								
Particulate wt. - total, mg	3,050	4,060	1,690	2,370	2,520	2,870	6,090	5,290
Part. load - ttl., std. cn., mg/nm^3	4,540	9,690	3,450	3,520	6,210	8,870	23,700	21,000
Part. load - ttl., std. cn., corrected to 12% CO_2, mg/nm^3	8,500	14,500	4,800	6,500	14,100	16,100	65,000	31,600
Part. load - ttl., stk. cn., mg/m^3	2,120	4,930	1,530	1,640	3,610	5,390	13,700	11,600
Partic. emis. - total, kg/hr	1.771	2.314	0.963	1.398	1.471	1.655	3.545	3.051
Percent impinger catch	9.45	22.97	9.55	9.68	18.42	15.77	7.98	0.84

Table 81. OPERATIONAL DATA SUMMARY--50% CAPTAN WETTABLE POWDER EXPERIMENTS

Run No.	A	B	C	D	E	F	G	H
Temperature °C (°F)								
Primary chamber (Thermocouple No. ①)	940 (1730)	890 (1640)	970 (1770)	930 (1700)	630 (1170)	640 (1180)	630 (1160)	670 (1240)
Primary chamber (Thermocouple No. ②)	940 (1730)	910 (1670)	950 (1740)	950 (1750)	570 (1060)	550 (1020)	560 (1040)	590 (1100)
Primary chamber (Thermocouple No. ③)	1000 (1830)	920 (1690)	1010 (1850)	980 (1790)	660 (1220)	670 (1230)	650 (1200)	690 (1280)
Second chamber (Thermocouple No. ④)	900 (1650)	790 (1450)	880 (1620)	870 (1590)	600 (1110)	580 (1080)	580 (1070)	600 (1110)
Second chamber (Thermocouple No. ⑤)	640 (1180)	530 (990)	630 (1160)	620 (1150)	430 (810)	390 (740)	390 (730)	390 (740)
Sample Point No. ② (Thermocouple No. ⑥)	390 (740)	290 (550)	370 (690)	380 (720)	240 (470)	210 (410)	210 (410)	210 (410)
Pressures								
Draft (Manometer No. △), pascals (in H_2O) gauge	58 (0.235)	27 (0.110)	30 (0.120)	51 (0.205)	25 (0.100)	16 (0.065)	16 (0.065)	16 (0.065)
Burner operation pressure, pascals (psi) gauge	7.4×10^5 (108)	7.5×10^5 (109)	7.4×10^5 (107)	7.7×10^5 (111)	7.4×10^5 (107)	7.4×10^5 (107)	7.4×10^5 (108)	7.4×10^5 (108)
Pesticide injection air, pascals (psi) gauge	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)
Scrubber liquids[a]								
1st Stage, H_2O scrubber								
Volume, ℓ (gal.)	1010 (268)	1060 (279)	1080 (286)	1020 (270)	1080 (286)	1100 (291)	1100 (291)	980 (259)
Captan conc., mg/ℓ	$< 2 \times 10^{-2}$[d]	$< 2 \times 10^{-3}$[d]	$< 2 \times 10^{-3}$[d]	NA	$< 2 \times 10^{-3}$[d]	NA	$< 2 \times 10^{-3}$[d]	NA
Total species conc.,[b] mg/ℓ	2×10^{-2}	1×10^{-1}	4×10^{-2}	NA	9×10^{-2}	NA	2×10^{-1}	NA
2nd Stage hexalene glycol scrubber								
Volume, ℓ (gal.)	104 (27.4)	100 (26.4)	101 (26.8)	103 (27.1)	99 (26.1)	98 (25.8)	104 (27.6)	93 (24.6)
Captan conc., mg/ℓ	$< 7 \times 10^{-3}$[d]	NA[e]	$< 7 \times 10^{-3}$[d]	ND[f]	$< 7 \times 10^{-3}$[d]	$< 7 \times 10^{-3}$[d]	$< 7 \times 10^{-3}$[d]	$< 7 \times 10^{-3}$[d]
Total species conc. change,[b] mg/ℓ	4×10^{-2}	NA	4×10^{-1}	ND	9×10^{-1}	ND	2×10^{-1}	2×10^{-1}
3rd Stage O scrubber								
Volume, ℓ (gal.)	1950 (514)	1950 (514)	1900 (503)	1730 (457)	2030 (537)	1900 (503)	1860 (491)	1730 (457)
Captan conc., mg/ℓ	$< 2 \times 10^{-4}$[d]	$< 2 \times 10^{-4}$[d]	$< 2 \times 10^{-3}$[d]	$< 2 \times 10^{-3}$[d]	$< 2 \times 10^{-3}$[d]	NA	$< 2 \times 10^{-3}$[d]	NA
Total species conc.,[b] mg/ℓ	1×10^{-3}	6×10^{-3}	3×10^{-2}	6×10^{-3}	6×10^{-3}	NA	6×10^{-3}	NA
Scrubber system								
Effluent gas (Sample Point No. ⑨)[c]								
Captan conc., mg/m^3	$< 3 \times 10^{-3}$[d]	$< 2 \times 10^{-3}$[d]	$< 3 \times 10^{-3}$[d]	$< 3 \times 10^{-3}$[d]	$< 2 \times 10^{-3}$[d]	$< 3 \times 10^{-3}$[d]	$< 2 \times 10^{-3}$[d]	$< 2 \times 10^{-3}$[d]
Total species conc.,[b] mg/m^3	4×10^{-2}	2×10^{-2}	1×10^{-2}	2×10^{-2}	2×10^{-2}	2×10^{-2}	1×10^{-1}	1×10^{-2}

---

[a] Scrubber water (Scrubbers 1 and 3) was used once through, while the hexylene glycol (Scrubber 2) was recycled. The concentrations reported for hexylene glycol, therefore, are the concentration changes (increases) detected during the respective tests.

[b] Captan plus all other chlorinated hydrocarbons species detected.

[c] As the wet gas at one atmosphere pressure, and 21.1°C (70°F).

[d] No captan detected. The values given represents the limit of detection for captan in the particular sample.

[e] No analysis.

[f] No increase detected.

The results of cyanide (CN^-) analysis of the incinerator off-gas are summarized as follows:

Run No.	Primary chamber temperature °C (°F)	Excess air %	Cyanide content[a]	
			mg/m^3	g/hr
A	1000 (1830)	137	77	30
B	920 (1690)	94	129	31
C	1010 (1850)	76	46	13
D	980 (1790)	135	49	19
E	660 (1220)	192	NA[b]	NA
F	670 (1230)	130	27	5
G	650 (1200)	252	107	16
H	690 (1280)	99	133	19

[a] Calculated as CN^-.
[b] No analysis.

These results show that significant amounts of cyanide were apparently generated* on all eight tests. No correlation has been found between the relative rate of cyanide generation (rate of cyanide generated to rate of captan incinerated) and any of the operating conditions being investigated (rate of pesticide injection, percent excess air, and operating temperature).

The results from particulate sampling of the captan tests are summarized in Table 80. All eight runs were within acceptable isokinetic limits. The 50% wettable powder formulation of captan follows the previously established trend of particulate emissions, which exceed established incinerator limits. The incineration of the captan formulation will, therefore, require a particulate emission control system.

DISCUSSION

No problems were encountered during the incineration of captan. It should be noted, however, that the H_2S-like odor was quite evident during experimental runs.

---

* The cyanide (CN^-) sample for the incinerator effluent gas from Test No. E was not recovered. However, analysis of the scrubber-system exhaust (Sample Point No. ⑨, Figure 5, p. 27) showed a cyanide concentration comparable to those from the other seven tests.

References

1. Martin, H., Pesticide Manual, 2nd ed., British Crop Protection Council, Worcester, England (1971).

2. Stauffer Chemical Company, "Technical Captan Data Sheet" (1965).

3. Merck Index, The, P. G. Strecher (ed.), 8th ed., Merck and Company, Rahway, New Jersey (1968).

4. Chevron Chemical Company, Ortho Technical Information Bulletin (April 1974).

5. von Rümker, R., and F. Horay, Pesticide Manual, Vol. I, Department of State, Agency for International Development (1972).

6. Melnikov, N. N., "Chemistry of Pesticides," Res. Rev., 36:247 (1971).

7. California Spray-Chemical Corporation, The Chemistry of Captan (31 March 1955).

8. U.S. Environmental Protection Agency, EPA Compendium of Registered Pesticides, Vol. III, Washington, D.C. (1973).

9. Midwest Research Institute, "Initial Scientific and Minieconomic Review of Captan" (Draft) EPA Contract No. 68-01-2448 (September 1974).

VIII. ZINEB

PESTICIDE DESCRIPTION

Physical Properties

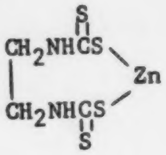
Chemical Name: Zinc ethylene bisdithiocarbamate

Common Name: Zineb

Trade Name: Aspor®, Chem Zineb®, Dithane® Z-78, Hexathane®, Kypzin®, Lonacol®, Pamosol 2 Forte®, Parzate® C, Polyram® Z, Tiezene®, Tritofterol®, Zebtox®, Zidan®, Zinosan®

Pesticide Class: Fungicide

Structural Formula:



Empirical Formula: $C_4H_6N_2S_4Zn$

Molecular Weight: 275.8

Physical State: Off-white solid

Solubility in:

Water: 10 ppm

Organic Solvents: Soluble in pyridine

Lipids, Fats: Negligible

Melting Point: Decomposes before melting

Vapor Pressure: Negligible at 15°C

Flammability: Flash point (open cup) between 138 and 143°C (280 and 290°F)

Stability: Decomposes gradually, accelerated by exposure to moisture, heat or air

Chemical Properties

Zineb is reported to be unstable toward moisture; acid hydrolysis yields CS_2.[1] Heating above 120°C is also reported to cause decomposition to a carbonaceous product.[2] Zineb is said to be the most stable of the metallic dithiocarbamates.[3]

Production and Use

Zineb is a fungicide used extensively on vegetable crops as well as on a few fruit crops.

Zineb is available commercially in wettable powder formulations varying in strength from 75 to 96% active ingredient.

Unpublished MRI estimates of domestic pesticide usage for 1972 include an estimate of 8 million pounds for zineb.

FORMULATIONS TESTED

A 75% wettable powder WP formulation was the only form tested. The WP was obtained from two manufacturers.

Zineb Wettable

Manufacturer: Ortho Division, Chevron Chemical Company, San Francisco, California

Composition: Active Ingredient

Zineb*	75%
Inert Ingredients	25%
Total	100%

Zinc expressed as metallic: 17.7%

---

* Zinc ethylene bisdithiocarbamate

Registration: EPA Reg. No. 239-523-AA

Lot No.: M21122-CK96

Particle Size Specification: Formulated from 882 parts technical material (85% zineb), 98 parts clay, and 20 parts dispersing agents such that > 99.9% pass a 149 μ (100 mesh) sieve with brushing

Zineb 75 Wettable Powder Fungicide

Manufacturer: Niagara Chemical Division, FMC Corporation, Middleport, New York

Composition: Active Ingredient

Zineb (zinc ethylene bisdithiocarbamate) (total zinc as metallic: 17.7)	75.0%
Inert Ingredients	25.0%
Total	100.0%

Particle Size Specification: At least 99% of the particles pass through a 44 μ (325 mesh) sieve

Registration: USDA Reg. No. 279-1387

PRELIMINARY THERMAL ANALYSIS

Bomb calorimetric analyses gave the following results.

Sample	Test	Test Method	Results
Technical Zineb	Sulfur	ASTM D-129	1.91%
	Heat of Combustion	ASTM D-2015	1.058×10^7 J/kg (4,554 Btu/lb)
Zineb Wettable Powder (75%)	Sulfur	ASTM D-129	1.05%
	Heat of Combustion	ASTM D-2015	2.168×10^7 J/kg (9,329 Btu/lb)

Figures 57 and 58 the results of DTA and TGA of the technical grade zineb (85%). DTA data show that decomposition of the sample starts at about 150°C, with two endotherms at about 160 and 290°C, respectively, and exotherms at about 190, 440, 530, and 600°C, respectively. The decomposition process is substantiated by the TGA data which indicate that about 80% of the sample weight is lost at 800°C. The weight loss agrees, within experimental error, with the percent composition of the technical grade zineb.

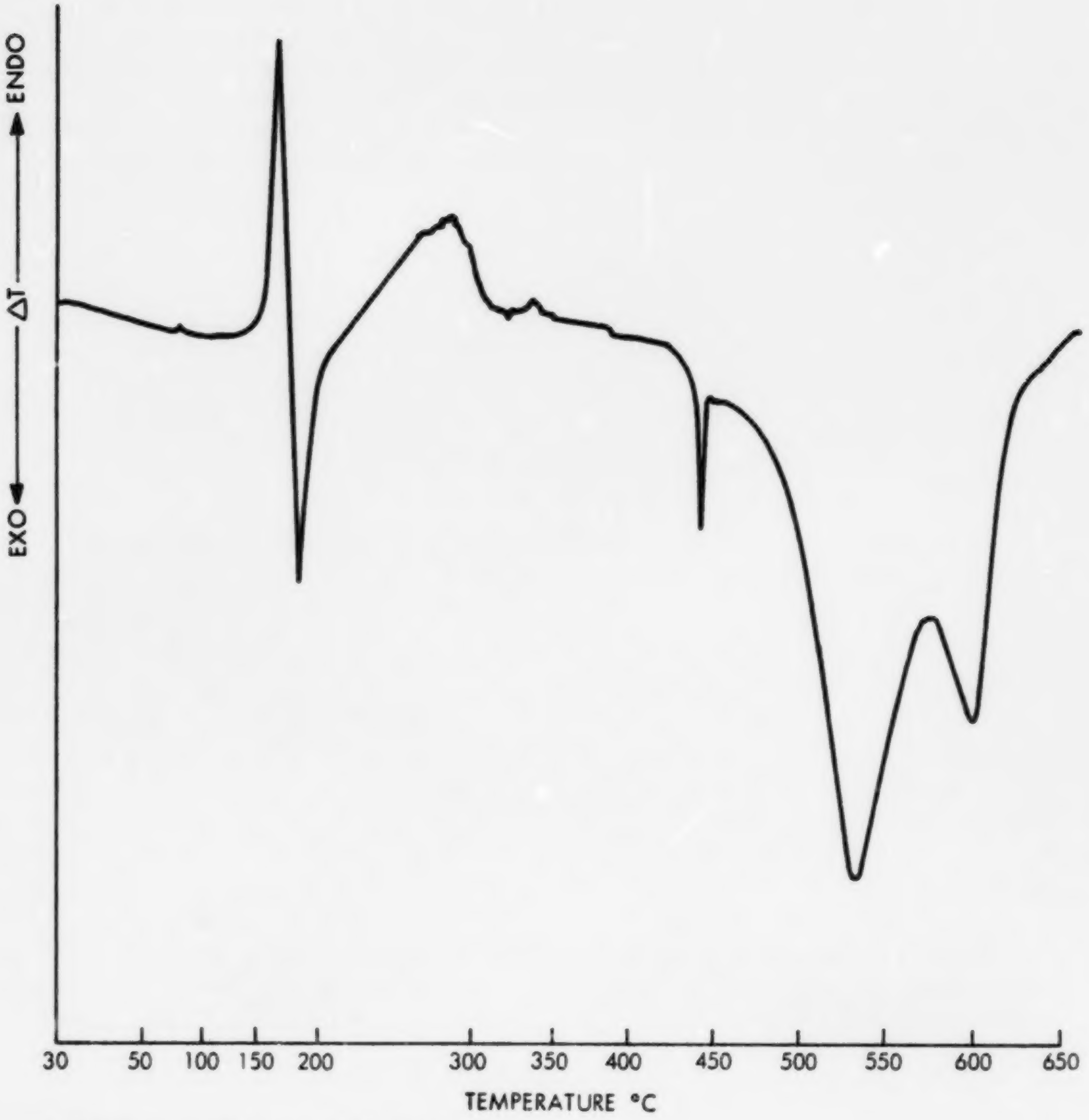
Figures 59 and 60 show the results of DTA and TGA data of the 75% wettable powder. DTA data show a similar decomposition pattern as that of the technical grade zineb, with characteristic endotherms at 170 and 260° respectively, and exotherms at 200, 440, 530, and 610°C, respectively. The decomposition process is substantiated by the TGA data which indicate that about 75% of the sample weight is lost at 800°C. The weight loss agrees very well with the percent composition of zineb in the formulation.

Kennedy et al. (1969)[4] also conducted DTA analysis of zineb. The results of their analyses were as follows:

	Endotherms	Exotherms
Reference Standard	185 and 496°C	196, 245, 525, 675, 690, 749, 767 and 795°C
75% WP Zineb formulation	187, 290, 390, 452 and 550°C	215, 232, and 620°C

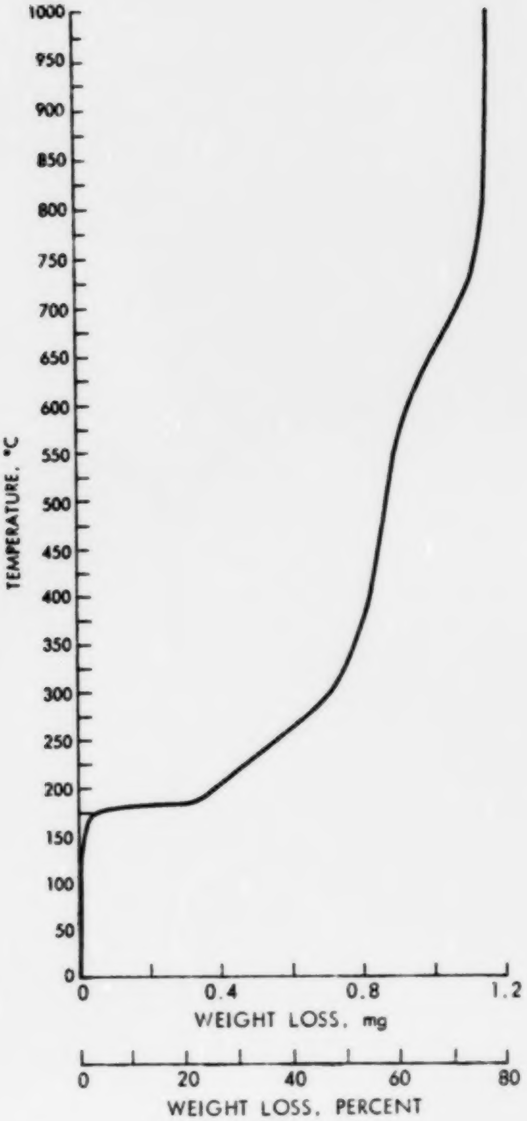
Sensitivity = 25%

Based on these and other laboratory analyses, Kennedy et al.[4] concluded that the temperature of complete combustion of the zineb reference standard and the 75% wettable powder formulation were 840°C (1544°F) and 690°C (1274°F), respectively.



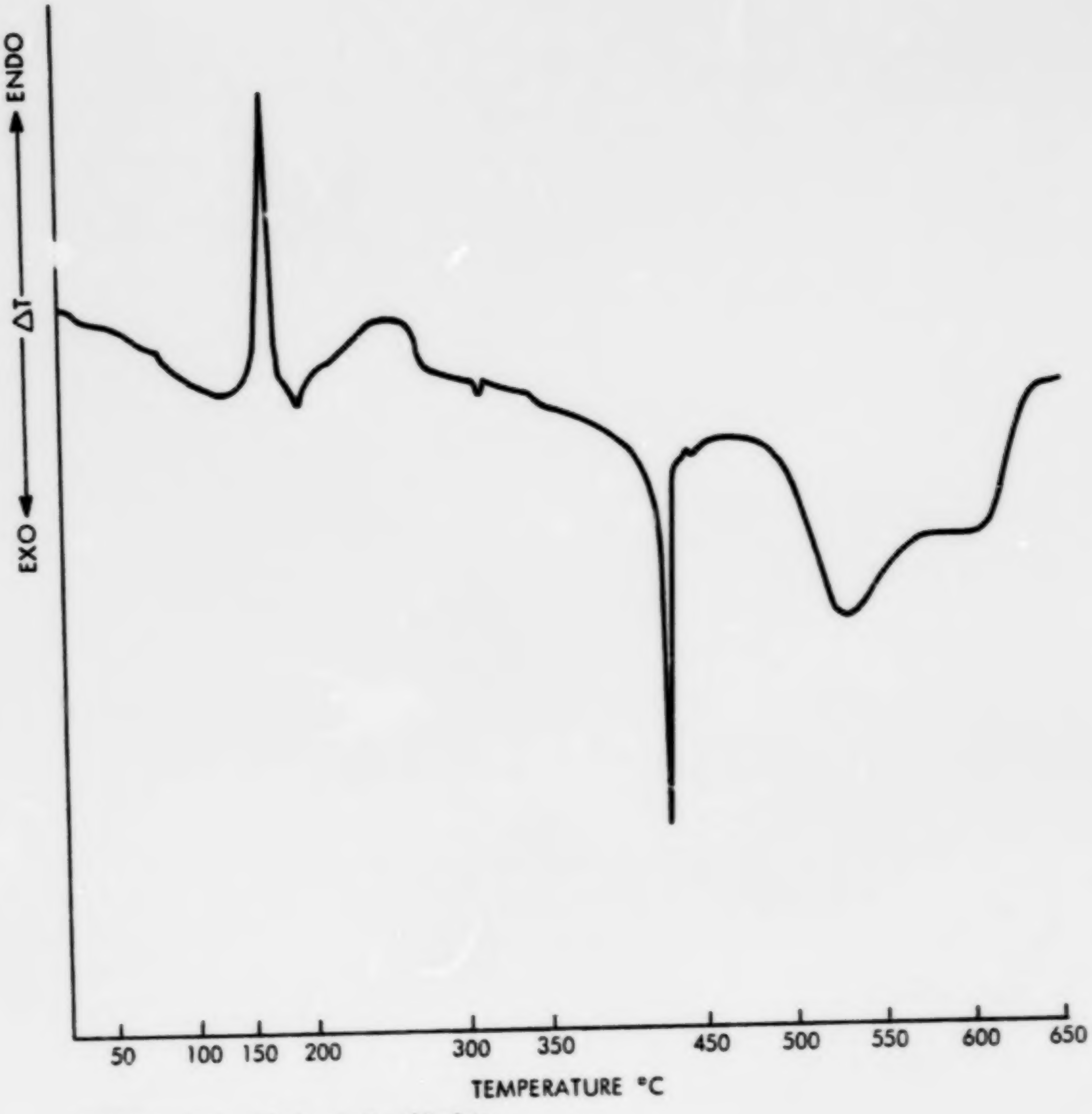
Reference: Al_2O_3 + Kaolinite
Prog. mode: Heat
Rate: 20°C/min
Start: 30°C

Figure 57. DTA of technical zineb



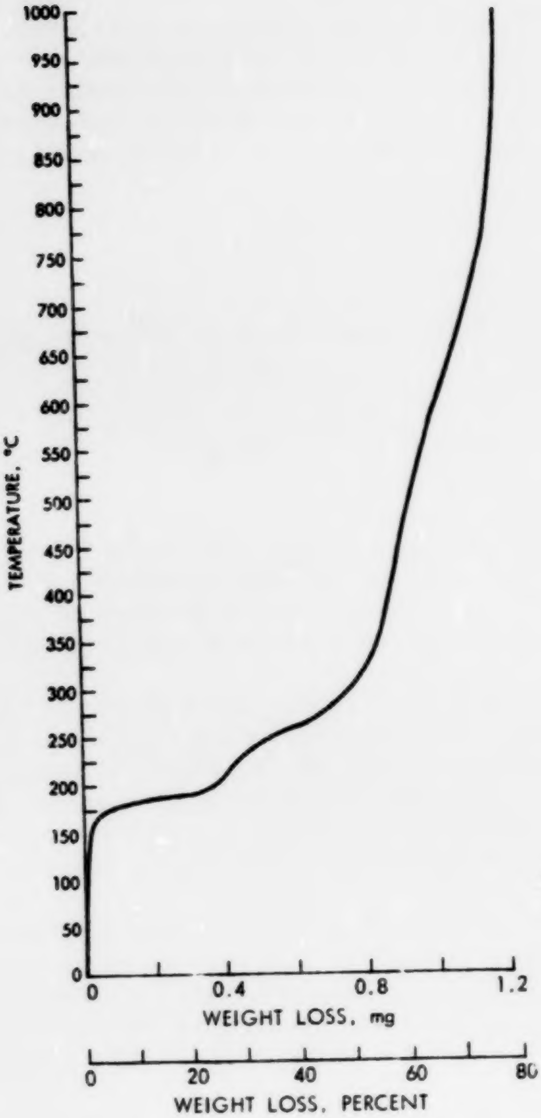
Sample weight: 1.504 mg
Heating rate: 20°C/min
Environment: ~ 20 ml/min air (20% O_2, 80% N_2)

Figure 58. TGA of technical zineb



Reference: Al_2O_3 + Kaolinite
Prog. mode: Heat
Rate: 20°C/min
Start: 40°C

Figure 59. DTA of 75% zineb wettable powder

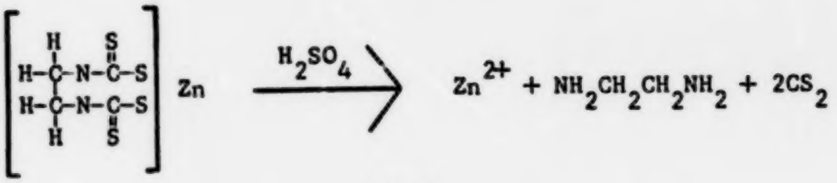


Sample weight: 1.540 mg
Heating rate: 20°C/min
Environment: ~ 20 ml/min air (20% O_2, 80% N_2)

Figure 60. TGA of 75% zineb wettable powder

METHODS OF ANALYSIS

Dithiocarbamate fungicides, e.g., maneb, nabam, and zineb, are nonvolatile compounds and are not subject to gas chromatographic analysis intact.[5] There are no published methods of analyses for trace quantities of zineb in the presence of extremely high quantities of ZnO as encountered in the incinerator sampling train. Existing methods of analysis for zineb rely on the analysis of degradation products resulting from the following reaction:



Zineb

The problem with this approach when analyzing incinerator effluents and residues is obvious--the incinerated sample can be expected to contain trace quantities of zineb and a wide range of various degradation products, depending on the efficiency of incineration.

After searching the literature and consulting EPA scientists at two laboratories, it was concluded that direct measurement of intact zineb at useful concentration levels was not possible within the time and cost limitations of this program. The most useful information that could be obtained concerning the effectiveness of incineration was the amount of organically bound zinc present in the various samples.

The approach used was to attempt to separate trace quantities of organic zinc by solvent extraction from high quantities of inorganic zinc, which resulted from incineration. The solubility of zineb in organic solvents is quite limited. Pyridine was selected as the solvent which might preferentially extract zineb in the presence of zinc oxide.

Synthetic mixtures of zineb and varying quantities of zinc oxide were extracted with pyridine. The pyridine extracts were evaporated to dryness, digested in acid, and the zinc determined by atomic absorption spectrometry (AAS). In the absence of zinc oxide, zineb could be determined quantitatively by this method. However, the excess zinc oxide resulted in a high, inconsistent background due to the extraction of this species into the pyridine.

Because zineb is soluble in relatively polar solvents, it is not likely that other solvents that would dissolve zineb would not dissolve zinc oxide also. Therefore, this approach was not investigated further.

The next approach investigated was to analyze for ethylenediamine (EDA) by gas chromatography (GC). Zineb standards could be quantitatively determined by GC of EDA but, similar to the AAS method, excess zinc oxide interfered. The interference was probably due to chelation of the EDA by the excess zinc. The resulting zinc/EDA complex could not be analyzed by GC.

Several methods were attempted to release the EDA for GC analysis. All were unsuccessful. Several of the methods are described below.

Destruction of the Complex with Heat

Samples were injected into the gas chromatograph at an elevated injection port temperature (up to 350°C).

Distillation

Distillation from basic aqueous solution was attempted in the hope of separating the EDA from the zinc. Although H_2O boils lower than EDA (116.5°C), EDA was recovered (at least 25%) from a synthetic EDA/Zn oxide mixture. Ten filter samples were analyzed without success. The residues from the aqueous distillation were taken up in xylene which has a boiling point similar to EDA (116°C). No EDA was detected in the distillate.

Displacement with Chelating Agents

Displacement of EDA using 8-hydroxyquinoline (Oxine--8-hydroxyquinoline) as a chelating agent was attempted in the hope that the zinc would be removed from EDA and the free EDA would be available for GC analysis. Both acidic and basic samples were extracted with 8-hydroxyquinoline in benzene. A yellow precipitate was formed indicating the formation of zinc oxinate. However, GC analysis of both layers gave negative results for EDA.

Addition of Arsenate

Zinc arsenate has a very low solubility product. Arsenate was added to the aqueous solution of the 10 filter samples in an attempt to precipitate zinc arsenate and free the EDA for GC analysis. EDA was not detected in any of the 10 samples treated with arsenate.

When all attempts to analyze for EDA failed, carbon disulfide, evolved by the addition of sulfuric acid, was analyzed. The headspace analysis technique for carbon disulfide was not attempted before the methods discussed above because other workers, who had successfully applied the method to ferbam and nabam, reported problems with the analysis of zineb.6/

Although a number of problems were encountered with the headspace method, a satisfactory method for zineb was developed. Unfortunately, the CS_2 in the filter samples that were used for EDA method was lost during the development effort and these samples could not be analyzed. All other samples were analyzed by the headspace procedure described below.

Apparatus

For gas chromatographic analysis a Tracor 550 gas chromatograph equipped with dual mode (sulfur and phosphorus) flame photometric detectors (Meloy, Inc., Springfield, Virginia) and a 6-ft, 4 mm I.D. stainless steel column (packed with 3% OV-1 on 100/110 mesh Gas Chrom Q from Supelco, Inc., Bellefonte, Pennsylvania) was used. Chromatographic operating conditions were: injector temperature, 160°C; column temperature, ambient; detector temperature, 170°C; carrier flow rate, 45 ml/min N_2; detector flow rate, 30 ml/min, O_2; 120 ml/min, H_2; and 40 ml/min, air.

A Hewlett-Packard 3380A integrator recorder was used to record the chromatograms.

Reagents and Materials

A 1.1 N H_2SO_4 solution (prepared by dilution of concentrated reagent grade from Mallinckrodt) was used for hydrolysis of zineb. Pesticide grade toluene (matheson, Coleman, Bell) was used to prepare standard carbon disulfide solutions (Fisher Certified Reagent). Headspace gases were measured in Pierce Hypo-vials stoppered with gray Hycar septa (Pierce Chemical Company, Rockford, Illinois). Standard zineb (86.9%) was used to evaluate the yield of carbon disulfide.

Procedure for Sample Preparation

Sample preparation depended on the types of sample. Water impingers were taken to dryness with a stream of air. The residue was extracted with pyridine which was taken to dryness in a Pierce Hypo-vial. The vial was stoppered, and 1 ml of 1.1 N H_2SO_4 was injected. The sample was placed in a steam bath and heated for 1 hr, after which the solutions were placed in a temperature bath at 52 ± 1°C. Just prior to analysis, the headspace pressure was equilibrated by puncturing the septa, and measuring the gas-water displacement from an inverted burette. While still in the temperature bath, a volume of the headspace was sampled with a gas-tight syringe and injected into the chromatograph.

The mass of collected particulates was determined for all elements of the sample train at Sample Point No. ② as follows. All were taken to dryness under a hood in clean, desiccated, tared 250 ml beakers and desiccated 2 days before final weighing. The residue was extracted with pyridine and taken to dryness in a Pierce Hypo-vial. Following this step, sample preparation and analysis were the same as that used for water solutions.

Hexylene glycol solutions (from the second stage scrubber) were treated as follows: 1 ml of the hexylene glycol solution was acidified with enough 1.1 N H_2SO_4 (approximately 1 ml) and then treated the same as water samples mentioned earlier.

Analysis and Discussion

The method for determination of zineb is based on headspace carbon disulfide analysis. At 100°C in 1.1 N H_2SO_4 the following reaction occurs:

$$\text{Zineb} \xrightarrow[100^\circ C]{H^+} 2\ CS_2 + NH_2CH_2CH_2NH_2 + Zn^{++}$$

Standard zineb treated as indicated yielded 85 to 95% of the theoretical amount of carbon disulfide.

The sensitivity of the instrument for carbon disulfide is 10 ng. Since 2 moles of carbon disulfide are generated for every mole of zineb, the sensitivity of the instrument for zineb is 5 ng.

Prior to adopting the headspace technique, determination of the ethylenediamine generated by the hydrolysis of zineb was investigated. A Perkin-Elmer 3920 gas chromatograph equipped with a phosphorus-nitrogen thermionic detector was used to follow the ethylenediamine peak. Zineb was detected at low nanogram levels from standard solutions. However, high zinc content in the incinerator samples prohibited use of this method (probably due to chelation of the ethylenediamine with zinc).

TEST CONDITIONS AND RESULTS

A total of 11 tests were conducted using the 75% zineb wettable powder. The results of these tests are given in Tables 82 through 86.

Table 82. SUMMARY OF 75% ZINEB WETTABLE POWDER EXPERIMENTS

Run No.	No. 2 fuel oil rate		Pesticide feed rate		Primary chamber temperature °C (°F)	Flame temperature[b] °C (°F)	Excess air[c] %	Retention time[d] sec		Sampling time min	Off-gas flow rate[e] m^3/hr (1,000's of SCFH)
	Nominal burner size ℓ/hr (gal/hr)	Actual rate ℓ/hr (gal/hr)	~ 75% Zineb formulation kg/hr (lb/hr)	Contained zineb[a] g/hr (lb/hr)				Primary chamber	Second chamber		
A	7.6 (2.0)	5.90 (1.56)	4.72 (10.4)	3540 (7.8)	890 (1630)	1000 (1830)	69	3.3	3.3	60	193 (6.8)
B	11.4 (3.0)	9.42 (2.49)	4.22 (9.3)	3180 (7.0)	970 (1770)	1080 (1980)	106	1.9	1.9	60	303 (10.7)
C	3.8 (1.0)	3.90 (1.03)	4.31 (9.5)	3220 (7.1)	680 (1260)	930 (1700)	102	5.2	5.1	60	150 (5.3)
D	3.8 (1.0)	3.79 (1.00)	3.40 (7.5)	2540 (5.6)	710 (1310)	930 (1700)	153	3.4	3.2	60	218 (7.7)
E	3.8 (1.0)	3.86 (1.02)	2.13 (4.7)	1590 (3.5)	690 (1270)	980 (1790)	111	5.0	4.8	60	156 (5.5)
F	3.8 (1.0)	3.79 (1.00)	2.31 (5.1)	1720 (3.8)	650 (1200)	990 (1820)	165	4.4	4.2	60	184 (6.5)
G	9.5 (2.5)	9.08 (2.40)	2.27 (5.0)	1680 (3.7)	980 (1790)	1060 (1940)	67	2.5	2.4	60	235 (8.3)
H	9.5 (2.5)	9.27 (2.45)	2.31 (5.1)	1720 (3.8)	940 (1730)	1090 (1990)	151	1.8	1.7	60	340 (12.0)
I	9.5 (2.5)	8.67 (2.29)	4.08 (9.0)	3040 (6.7)	1000 (1830)	1050 (1920)	62	2.4	2.3	60	235 (8.3)
J	9.5 (2.5)	9.42 (2.49)	4.76 (10.5)	3580 (7.9)	930 (1710)	990 (1820)	129	1.9	1.7	60	337 (11.9)
K	4.7 (1.25)	4.43 (1.17)	2.81 (6.2)	2130 (4.7)	710 (1310)	990 (1810)	85	5.1	4.9	60	150 (5.3)

---

a/ Nominal zineb content of the ~ 75% zineb wettable powder formulation.

b/ The flame temperature was observed at a point approximately 15 cm (6 in.) in from the front wall of the incinerator.

c/ Calculated according to Method 3 of "Standards of Performance for New Stationary Sources," Federal Register, 36(247):24876-24895, 23 December 1971.

d/ Retention time is defined as $\frac{V}{v}$, where v is the wet off-gas flow rate from the incinerator at the respective chamber temperature and pressure, and V is the volume of that chamber.

e/ As dry gas at one atmosphere pressure, and 21.1°C (70°F).

Table 83. RESIDUE CHARACTERISTICS--75% ZINEB WETTABLE POWDER EXPERIMENTS

Run No.	Pesticide feed rate		Solid residues				Ratio of total incinerator residue to total charge	Zineb content of the solid residues g/hr	Approximate ratio of zineb in off-gas to zineb fed	Incineration efficiency d/ %
			Primary chamber		Second chamber					
	~ 75% WP formulation kg/hr (lb/hr)	Contained zineb a/ g/hr	Total g/hr	Zineb conc. ppm	Total g/hr	Zineb conc. ppm				
A	4.72 (10.4)	3,540	200	14.8	116	15	0.067	4.7×10^{-3}	4×10^{-5}	> 99.99
B	4.22 (9.3)	3,180	122	11	79	NA b/	0.048	1.3×10^{-3} c/	3×10^{-5}	> 99.99
C	4.31 (9.5)	3,220	124	16	56	19.2	0.042	3.1×10^{-3}	3×10^{-5}	> 99.99
D	3.40 (7.5)	2,540	97	14.5	34	13.1	0.038	1.8×10^{-3}	3×10^{-5}	> 99.99
E	2.13 (4.7)	1,590	57	34	26	< 0.2	0.039	1.9×10^{-3}	3×10^{-5}	> 99.99
F	2.31 (5.1)	1,720	55	< 2	47	< 1	0.044	$< 1.6 \times 10^{-3}$	3×10^{-5}	> 99.99
G	2.27 (5.0)	1,680	54	< 1	20	4.6	0.033	$< 1.5 \times 10^{-4}$	4×10^{-7}	> 99.99
H	2.31 (5.1)	1,720	38	0.8	25	< 0.2	0.027	3.5×10^{-5}	4×10^{-7}	> 99.99
I	4.08 (9.0)	3,040	28	1.2	40	< 0.9	0.017	7.0×10^{-5}	3×10^{-6}	> 99.99
J	4.76 (10.5)	3,580	25	< 1.2	76	5.4	0.021	4.4×10^{-4}	1×10^{-5}	> 99.99
K	2.81 (6.2)	2,130	40	8.3	24	16.1	0.023	7.2×10^{-4}	1×10^{-6}	> 99.99

---

a/ Nominal zineb content of the ~ 75% wettable powder formulation.

b/ No analysis.

c/ Does not include any zineb present in the second chamber residue.

d/ Efficiency is defined as $\left[1 - \frac{\text{quantity } \underline{\text{out}}}{\text{quantity } \underline{\text{in}}}\right] \times 100$, where the quantity out is evaluated at Sample Points Nos. ② (incinerator off-gas) and ③ (incinerator residues), and the quantity in is evaluated at Sample Point No. ① (the incinerator feed).

Table 84. OFF-GAS COMPOSITION--75% ZINEB WETTABLE POWDER INCINERATION[a]

Run No.	Zineb[b] mg/m^3	CN$^-$ mg/m^3	SO$_2$ mg/m^3	NO$_x$[c] mg/m^3	Total hydrocarbons analyzer: Total hydrocarbons ppm	Total hydrocarbons analyzer: CO ppm	Total hydrocarbons analyzer: CH$_4$ ppm	Orsat analyzer: O$_2$ vol. %	Orsat analyzer: CO$_2$ vol. %	Orsat analyzer: CO vol. %	Moisture vol. %
A	1	1,260	21,800	37	5	6	< 1	8.8	8.9	0.0	6.9
B	0.3	617	8,330	185	2	ND[d]	< 1	11.2	6.7	0.0	6.7
C	0.7	1,100	22,900	21	< 1	2	< 1	10.9	7.3	0.0	6.7
D	0.4	703	14,500	13	5	< 1	< 1	12.9	5.9	0.0	8.5
E	0.3	668	13,100	19	5	< 1	< 1	11.4	7.0	0.0	6.3
F	0.3	835	12,500	9	10	< 1	< 1	13.3	5.7	0.0	5.3
G	0.003	707	8,140	113	2	< 1	ND	8.7	9.0	0.0	6.4
H	0.002	138	6,670	125	4	ND	ND	12.9	5.9	0.0	6.4
I	0.04	569	12,900	96	4	ND	ND	8.3	9.2	0.0	8.4
J	0.1	768	10,300	321	4	< 1	< 1	12.1	6.4	0.0	6.7
K	0.07	1,080	20,500	68	5	ND	< 1	9.9	8.2	0.0	6.4

---

[a] As dry gas at one atmosphere pressure, and 21.1°C (70°F).
[b] Approximated value.
[c] Calculated as NO$_2$.
[d] Not detected.

Table 85. OPERATIONAL DATA SUMMARY--75% ZINEB WETTABLE POWDER EXPERIMENTS

Run No.	A	B	C	D	E	F
Temperature °C (°F)						
Primary chamber (Thermocouple No. ①)	860 (1580)	930 (1710)	650 (1200)	670 (1240)	670 (1240)	630 (1170)
Primary chamber (Thermocouple No. ②)	850 (1570)	900 (1660)	590 (1100)	600 (1110)	620 (1140)	570 (1050)
Primary chamber (Thermocouple No. ③)	890 (1630)	970 (1770)	680 (1260)	710 (1310)	690 (1270)	650 (1200)
Second chamber (Thermocouple No. ④)	750 (1390)	850 (1560)	590 (1090)	630 (1160)	600 (1120)	580 (1080)
Second chamber (Thermocouple No. ⑤)	520 (970)	610 (1130)	380 (720)	430 (800)	400 (760)	390 (730)
Sample Point No. ② (Thermocouple No. ⑥)	260 (500)	370 (690)	200 (400)	230 (450)	190 (380)	210 (410)
Pressures						
Draft (Manometer No. △), pascals (in. H_2O) gauge	16 (0.065)	42 (0.170)	12 (0.050)	24 (0.095)	12 (0.050)	24 (0.095)
Burner operation pressure, pascals (psi) gauge	7.4×10^5 (108)	7.4×10^5 (108)	7.5×10^5 (109)	7.7×10^5 (112)	7.4×10^5 (108)	7.4×10^5 (108)
Pesticide injection air, pascals (psi) gauge	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)

Run No.	G	H	I	J	K
Temperature °C (°F)					
Primary chamber (Thermocouple No. ①)	940 (1720)	890 (1640)	950 (1760)	880 (1620)	690 (1270)
Primary chamber (Thermocouple No. ②)	920 (1690)	850 (1560)	930 (1710)	850 (1570)	590 (1100)
Primary chamber (Thermocouple No. ③)	980 (1790)	940 (1730)	1000 (1830)	930 (1710)	710 (1310)
Second chamber (Thermocouple No. ④)	870 (1590)	870 (1600)	890 (1630)	850 (1560)	630 (1170)
Second chamber (Thermocouple No. ⑤)	640 (1190)	640 (1190)	630 (1160)	600 (1110)	420 (780)
Sample Point No. ② (Thermocouple No. ⑥)	350 (660)	380 (710)	340 (630)	380 (710)	210 (410)
Pressures					
Draft (Manometer No. △), pascals (in. H_2O) gauge	24 (0.095)	56 (0.225)	24 (0.095)	51 (0.205)	12 (0.050)
Burner operation pressure, pascals (psi) gauge	7.4×10^5 (108)	7.4×10^5 (107)	7.4×10^5 (107)	7.4×10^5 (108)	7.4×10^5 (107)
Pesticide injection air, pascals (psi) gauge	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)

Table 86. PARTICULATE SAMPLING SUMMARY--75% ZINEB WETTABLE POWDER EXPERIMENTS

Description	A	B	C	D	E	F	G	H	I	J	K
Vol. dry gas - std. cond., nm^3	0.343	0.521	0.260	0.392	0.262	0.310	0.413	0.587	0.423	0.577	0.255
Percent moisture by vol.	6.9	6.7	6.7	6.5	6.3	5.3	6.4	6.4	8.4	6.7	6.4
Avg. stack temperature, °C	243.8	356.7	191.5	191.5	175.3	202.1	354.9	377.1	354.6	351.6	203.5
Stk. flow rate, dry, std. cond., nm^3/min	3.2	5.0	2.5	3.6	2.6	3.1	3.9	5.7	3.9	5.6	2.5
Actual stack flow rate, m^3/min	6.0	11.7	4.2	6.2	4.2	5.3	8.9	13.3	9.2	12.6	4.3
Percent isokinetic	101.8	98.7	98.1	103.0	97.3	97.0	100.8	99.4	102.7	98.6	97.7
Percent excess air	70	107	102	155	112	165	67	151	62	129	85
Particulates - partial catch											
Particulate wt. - partial, mg	2,860	2,501	2,000	2,200	793	1,360	1,470	1,600	2,580	2,310	1,740
Part. load - ptl., std. cond., mg/nm^3	8,320	4,790	7,680	5,590	3,030	4,380	3,550	2,710	6,090	4,000	6,810
Part. load - ptl., stk. cond., mg/m^3	4,430	2,070	4,580	3,260	1,860	2,540	1,570	1,150	2,600	1,780	3,940
Partic. emis. - partial, kg/hr	1.608	1.452	1.166	1.221	0.467	0.806	0.835	0.920	1.441	1.344	1.019
Particulates - total catch											
Particulate wt. - total, mg	3,350	2,730	2,440	2,860	1,100	2,020	2,220	2,430	3,450	3,420	2,400
Part. load - ttl., std. cond., mg/nm^3	9,760	5,240	9,370	7,270	4,210	6,480	5,380	4,130	8,130	5,910	9,390
Part. load - ttl., std. cn., corrected to 12% CO_2, mg/nm^3	13,200	9,400	15,400	14,800	7,200	13,600	7,200	8,400	10,600	11,100	13,700
Part. load - ttl., stk. cond., mg/m^3	5,190	2,260	5,590	4,240	2,580	3,760	2,380	1,760	3,480	2,630	5,430
Partic. emis. - total, kg/hr	1.885	1,587	1.423	1.589	0.651	1.190	1.264	1.401	1.924	1.984	1.404
Percent impinger catch	14.70	8.53	18.09	23.19	28.19	32.41	33.97	34.32	25.10	32.26	27.43

As has been discussed in the preceding subsection on analytical methods, the zineb analyses are not comparable to those of the eight other pesticides tested. This is due in general to the limitations in the available zineb analytical methods, and in particular to the inability to analyze the filter element of the off-gas sampling train. However, an approximation of the zineb content of the particulates trapped on the filter element can be made by utilizing the analyses for other residue samples obtained after the completion of each test. These additional samples were obtained from the walls of the horizontal and vertical sections of the incinerator stack preceding Sample Point No. ②, the normal incinerator off-gas sampling point. Values of the zineb content of the residues deposited in this section of the stack (average value of 55 ppm, ranging from < 0.2 to 109 ppm for the 11 tests) have been substituted for the filter element analyses in order to develop the estimated zineb quantities and concentrations given in Tables 83 and 84. Using this approximation, efficiencies of combustion have been calculated as > 99.99% for all 11 tests. It should be noted that the actual zineb content of the particulate material on the filter element of the off-gas sampling train would have to be greater than twice the highest incinerator-stack-residue zineb concentration detected (i.e., 2 x 109 or 218 ppm) before the efficiency of combustion would be less than that indicated, i.e., > 99.99%.

High cyanide levels were detected in the incinerator off-gas (Sample Point No. ②, for all zineb tests. The results of cyanide analyses, expressed as CN^-, are summarized as follows:

Run No.	Primary chamber temperature (°F)	Excess air (%)	Cyanide content (g/hr)	
			(g/hr)	(mg/m^3)
A	890 (1630)	69	243	1,260
B	970 (1770)	106	187	617
C	680 (1260)	102	165	1,100
D	710 (1310)	153	153	703
E	690 (1270)	111	104	668
F	650 (1200)	165	154	835
G	980 (1790)	67	166	707
H	940 (1730)	151	469	138
I	1000 (1830)	62	134	569
J	930 (1710)	129	259	768
K	710 (1310)	85	162	1,080

The results of the particulate sampling conducted on the zineb tests are given in Table 86. Acceptable isokinetic conditions were achieved on all runs. The particulate loadings all exceed what can be considered low emissions and indicate the need for particulate control devices when zineb wettable powder formulations are incinerated.

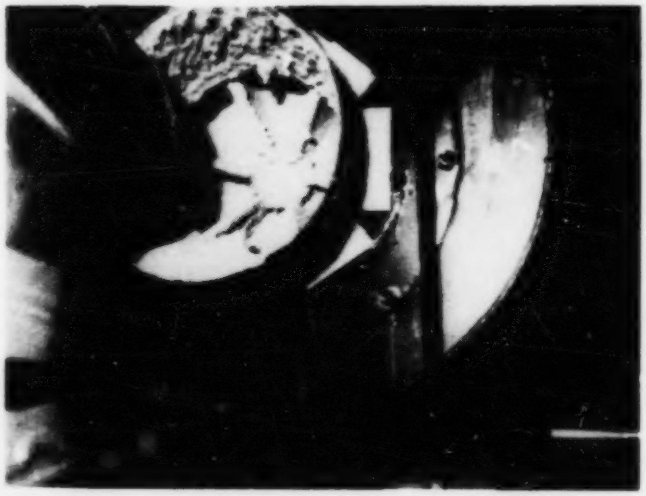
DISCUSSION

The most significant operational problem with the zineb incinerator was the inability of the off-gas scrubber system to clean up the effluent gas. A white plume was discharged from the scrubber system exhaust (Sample Point No. ⑨, the opacity of which ranged from 0 to 45%, based on random observations (see Figure 61a). The particulate material was also deposited on interior surface areas throughout the scrubber system. Residue deposition inside the scrubber system blower, as shown in Figure 61b, caused blower vibration during the latter tests.

The deposition of particulate material also caused plugging of the demister pads in the first and second stage scrubbers. The demister pad was removed from the second stage hexylene glycol scrubber after Run No. E in order to reduce plugging of the system. (The opacities of the exhaust plume for Runs Nos. A through E ranged from 0 to 20%, while those for Runs Nos. F through K ranged from 5 to 45%.)

The odor of SO_2 was also noted during the incineration of zineb.

a. Effluent plume (35% opacity)



b. Residue deposition in blower

Figure 61. Particulate discharge during zineb incineration

References

1. Martin, H., Pesticide Manual, British Crop Protection Council, Worcester, England (1971).

2. Melnikov, N. N., Chemistry of Pesticides, Springer-Verlag, New York, New York (1971).

3. 1975 Farm Chemicals Handbook, Meister Publishing Company, Willoughby, (1975).

4. Kennedy, M. V., B. J. Stojanovic, and F. L. Shuman, Jr., "Chemical and Thermal Methods for Disposal of Pesticides," Residue Reviews, **29**:95 (1969).

5. Zweig, G., and J. Sherma, "Analytical Methods for Pesticides and Plant Growth Regulators," Gas Chromatographic Analysis, Vol. VI, G. Zweig, ed., Academic Press, New York (1972).

6. McLeod, H. A., and K. A. McCully, J. AOAC, **52**(6):1226 (1969).

IX. MIREX

PESTICIDE DESCRIPTION

Physical Properties

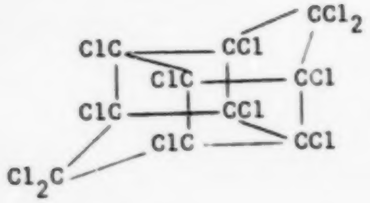
Chemical Name: Dodecachlorooctahydro-1,3,4-metheno-2H-cyclobuta (cd) pentalene

Common Name: Mirex

Trade Name: Dechlorane®, GC-1283

Pesticide Class: Stomach insecticide

Structural Formula:



Empirical Formula: $C_{10}Cl_{12}$

Molecular Weight: 545.6

Physical State: White crystalline solid

Melting Point: ~ 485°C

Flash Point: Nonflammable

Solubility: Insoluble in water; reasonably soluble dioxane, xylene, benzene, and carbon tetrachloride.

Chemical Properties

This highly chlorinated compound is reported to be unaffected by mineral acids (HCl, HNO_3 and H_2SO_4).[1] Lawless et al.[2] stated that mirex would be expected to be extremely resistant to oxidation except at the high temperature of an efficient incinerator.

Production and Use

Mirex is a stomach insecticide toxic to grass-feeding insects, especially ants. It is available in a limited number of solid bait formulations, the most important of which is a 0.3% mirex bait for Imported Fire Ant control. The use of mirex in the Fire Ant eradication program in the southeastern United States is currently the subject of review of EPA and USDA.

Unpublished MRI estimates of 1972 domestic pesticide use include an estimated 0.3 million pounds of mirex (as active ingredient).

FORMULATIONS TESTED

Mirex is commercially available in only solid formulations. A 0.3% bait, the principal form in which mirex is marketed, was the only formulation tested.

0.3% Mirex Bait

Name: Mirex Granulated Bait 4X

Manufacturer: Allied Chemical Corporation, Agricultural Division,
Morristown, New Jersey

Composition: Active Ingredient

Dodecachlorooctahydro-1,3,4-metheno-2H-cyclobuta(*cd*)pentalene*	0.3%
Inert Ingredients	99.7%
Total	100.0%

Registration: EPA Reg. No. 218-565

Lot No.: 2J1037

Particle Size Distribution: Mirex in soybean oil on 12/30 corncob grit (< 1.41 mm, > 595 μ)

---

* Mirex

PRELIMINARY THERMAL ANALYSIS

Laboratory thermal analyses were conducted on the 0.3% bait formulation as well as on technical mirex. Bomb calorimetric analyses gave the following results:

Sample	Test	Test Method	Result
Technical mirex	Heat of combustion	ASTM D-2015	1.058×10^7 J/kg (4,554 Btu/lb)
	Sulfur	ASTM D-129	1.91%
0.3% mirex bait formulation	Heat of combustion	ASTM D-2015	2.168×10^7 J/kg (9,329 Btu/lb)
	Sulfur	ASTM D-129	1.05%

Figures 62 and 63 show the results of DTA and TGA of the technical grade mirex (97%). DTA data show that decomposition of the sample starts at about 130°C, with two endotherms at about 140 and 370°C, respectively, and an exotherm at about 570°C. The decomposition process is substantiated by the TGA data which indicate that about 95% of the sample weight is lost at about 350°C, and almost all the sample is gone at 800°C.

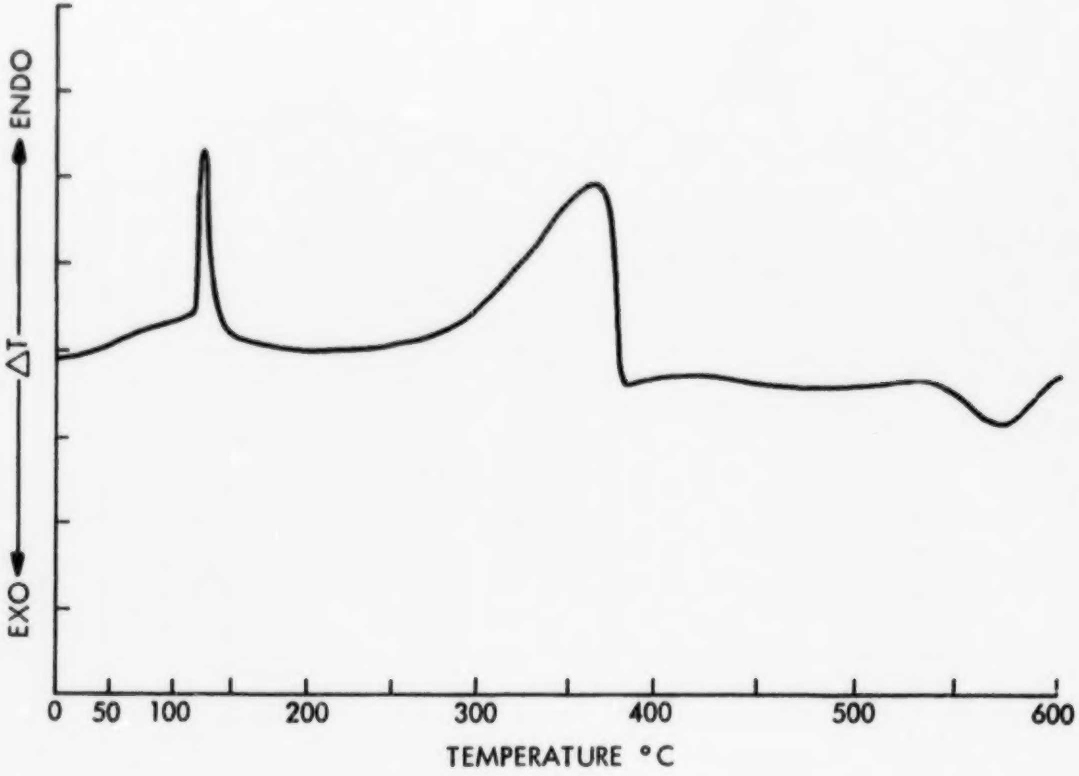
No DTA and TGA experiments were performed on the bait formulation because of the small amount of mirex present (0.3%).

METHODS OF ANALYSIS

Apparatus

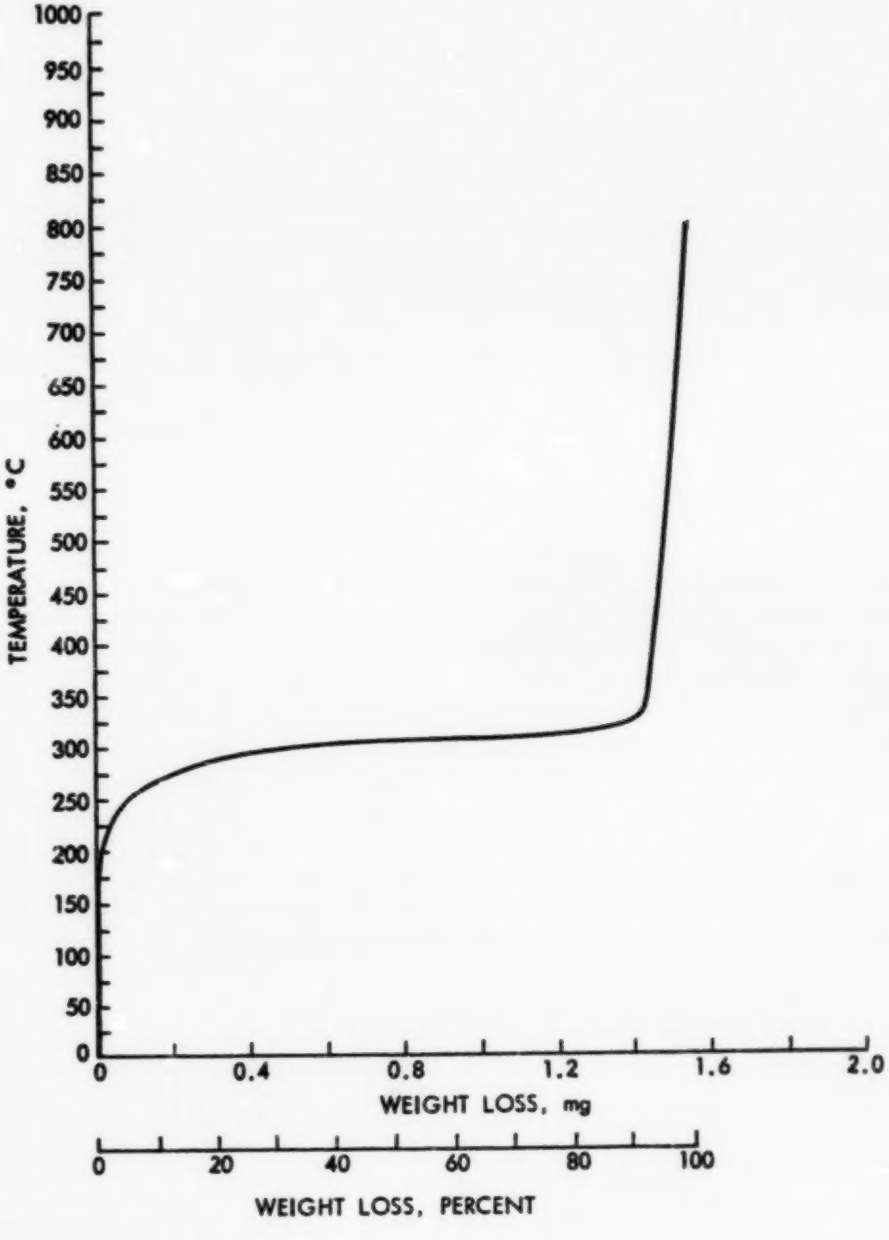
A Micro-Tek 2000R gas chromatograph equipped with a 3-ft, 4 mm I.D. glass column (packed with 1.5% OV-17 + 1.95% QF 1 on 80/100 mesh Supelcoport from Supelco, Inc., Bellefonte, Pennsylvania) and a tritium electron capture detector, maintained at a voltage of 18 V DC was used for gas chromatographic analysis. Chromatographic operating conditions were: injector temperature, 235°C; column temperature, 220°C; detector temperature, 180°C; carrier flow rate, 125 ml/min, N_2; and purge gas flow rate, 200 ml/min, N_2.

A Hewlett-Packard 3380A Integrator was used for peak identification and quantification.



Reference: Al_2O_3 + Kaolinite
Prog. mode: Heat
Rate: 20°C/min
Start: 0°C

Figure 62. DTA of technical mirex



Sample Weight: 1.518 mg
Heating Rate: 20°C/min
Environment: ~ 20 ml/min air (20% O_2, 80% N_2)

Figure 63. TGA of technical mirex

Reagents and Materials

The analytical reagent mirex (99.9%) was used for preparing standard solutions. Solvents used were pesticide grade benzene (Fisher Scientific) for all impingers and standard mirex solutions, and pesticide grade hexane (Matheson, Coleman, Bell) for extraction of hexylene glycol traps (from the second stage scrubber). All glassware coming from the laboratory (vials, beakers, etc.) was washed with Alconox Detergent (Scientific Products) and rinsed with deionized distilled water and reagent grade acetone (Fisher Scientific).

Standards and Calibration Curve

The solid standard, mirex, provided by USEPA, was used to prepare a stock solution of 100 μg/ml mirex and various dilutions were made to obtain linear results (linear range used: 0 to 2.50 ng).

Procedure for Sample Preparation

The mass of collected particulates was determined for all components of the Sample Point No. 2 train as follows. All samples were taken to dryness under a hood in clean, dessicated, tared 250-ml beakers and desiccated 2 days before final weighing. The residue was extracted with benzene (two 10- to 15-ml portions) and the extract taken just to dryness and capped tightly. Silica gel was extracted with just enough benzene to cover silica gel and a 20-ml portion pipetted out and taken just to dryness. Twenty milliliter portions of blank impinger solutions (benzene and acetone) were also pipetted into vials and taken just to dryness. All other impinger, wash and blank solutions, were taken just to dryness in the French Squares bottles as received. Ten milliliters of the hexylene glycol were extracted with n-hexane and the extract was taken just to dryness. All samples were taken up in appropriate amounts of benzene just prior to GC analysis.

Portions of all cleanout samples labeled (primary chamber, secondary chamber, etc.) were weighed out and extracted and the extracts were analyzed for mirex.

Analysis and Discussion

All samples were analyzed for mirex. Unidentified chromatographic peaks were quantitated against the mirex calibration curve.

The sensitivity of the instrument for mirex is 50 pg. Based on this sensitivity, and with a 5 µl sample injection for each analysis, the minimum detectable quantity for a 20-ml sample solution is 0.2 µg. However, during the analysis, samples were very often concentrated down to 1 ml which resulted in a minimum detectable quantity of 10 ng.

TEST CONDITIONS AND RESULTS

Ten tests were made using a 0.3% mirex bait formulation. This bait, the primary form in which mirex is used, is formulated on a combustible, granular carrier (i.e., corncob grit). Because of the size of the incinerator [designed for 45.4 kg/hr (100 lb/hr) of Type 1 waste, equivalent to 6.86 10^8 J/hr (650,000 Btu/hr)], the heat of combustion of the mirex bait formulation 2.168 x 10^7 J/kg (9,329 Btu/lb), and the low concentration of mirex (~ 0.3%), low rates of active ingredient injection were used. Mirex (as the pure active ingredient) was injected at nominal rates of 68 g/hr (0.15 lb/hr) and 34 g/hr (0.075 lb/hr), rather than the 3.40 kg/hr (7.5 lb/hr) and 1.70 kg/hr (3.75 lb/hr) rates used for all other pesticides studied.

The operational data for these 10 tests are summarized in Tables 87 through 91. Two efficiencies were calculated for the incineration of mirex, based on (a) the mirex content of the effluent gas and solid residues, and (b) the total chlorinated organic species (mirex plus all other chlorinated organic species) detected in the effluent gas and solid residues (see Table 88). Efficiency based on mirex content only ranged from > 98.21 to > 99.98% while efficiency based on total chlorinated organic species detected ranged from > 97.78 to > 99.96%. Both of these ranges are significantly lower than those for the other pesticides studied.

The temperature reported in Table 87 is the higher temperature in the upper portion of the primary chamber, i.e., Thermocouples Nos. 1 or 3 (see Figure 11, p. 91). Reference to the data in Table 90 will show that the temperature for Thermocouple No. 2 (located approximately 15 cm (6 in.) above the center of the primary chamber floor) was normally higher than either Thermocouples Nos. 1 or 3. This temperature (Thermocouple No. 2), however, is not representative of the chamber temperature. The mirex formulation, upon injection into the chamber, was observed to drop to the floor and continue to burn in close proximity of Thermocouple No. 2, thus giving a high temperature reading.

Table 87. SUMMARY OF 0.3% MIREX BAIT EXPERIMENTS

	No. 2 fuel oil rate		Pesticide feed rate					Retention time sec[d]			
Run No.	Nominal burner size ℓ/hr (gal/hr)	Actual rate ℓ/hr (gal/hr)	~ 0.3% Mirex bait kg/hr (lb/hr)	Contained Mirex[a] g/hr	Primary chamber temperature °C (°F)	Flame temperature[b] °C (°F)	Excess air[c] %	Primary chamber	Second chamber	Sampling time min	Off-gas flow rate[e] m^3/hr (1,000's of SCFH)
A	3.8 (1.0)	3.94 (1.04)	23.95 (52.8)	72	900 (1650)	1020 (1860)	57	2.8	3.0	60	263 (9.3)
B	2.8 (0.75)	2.73 (0.72)	23.36 (51.5)	70	870 (1600)	990 (1820)	85	2.6	2.8	60	300 (10.6)
C	5.7 (1.5)	5.75 (1.52)	23.00 (50.7)	69	930 (1710)	1020 (1860)	82	2.0	2.0	60	382 (13.5)
D	2.8 (0.75)	2.80 (0.74)	10.61 (23.4)	32	590 (1090)	1020 (1860)	225	2.8	3.4	60	297 (10.5)
E	2.8 (0.75)	2.84 (0.75)	10.80 (23.8)	32	700 (1290)	1020 (1860)	79	6.0	6.2	60	161 (5.7)
F	7.6 (2.0)	5.75 (1.52)	11.02 (24.3)	33	820 (1510)	1070 (1960)	48	5.3	5.5	60	167 (5.9)
G	9.5 (2.5)	9.50 (2.51)	11.52 (25.4)	35	940 (1730)	1090 (2000)	118	2.0	2.0	60	388 (13.7)
H	5.7 (1.5)	5.87 (1.55)	23.18 (51.1)	70	880 (1620)	1060 (1940)	123	1.7	1.6	60	456 (16.1)
I	2.8 (0.75)	2.84 (0.75)	22.59 (49.8)	68	760 (1400)	1020 (1860)	149	2.2	2.2	60	394 (13.9)
J	9.5 (2.5)	9.46 (2.50)	10.84 (23.9)	33	920 (1690)	1100 (2020)	141	1.8	1.5	60	428 (15.1)

---

a/ Analysis of grab samples of the bait formulation showed mirex content ranging from 0.21 to 0.41%. Because of the difficulty in obtaining representative samples of the material burned during each test (i.e., ~ 45.4 kg (100 lb) of a rather heterogeneous mixture), the nominal value of 0.3% mirex was used to calculate the quantity of contained mirex.

b/ The flame temperature was observed at a point approximately 15 cm (6 in.) in from the front wall of the incinerator (see Figure B-1).

c/ Calculated according to Method 3 of "Standards of Performance for New Stationary Sources," Federal Register, 36(247):24876-24895, 23 December 1971.

d/ Retention time is defined as $\frac{V}{v}$, where v is the off-gas flow rate from the incinerator at the respective chamber temperature and pressure, and V is the volume of that chamber.

e/ As dry gas at one atmosphere pressure, and 21.1°C (70°F).

Table 88. RESIDUE AND OFF-GAS CHARACTERISTICS--0.3% MIREX BAIT EXPERIMENTS

	Pesticide feed rate		Solid residue						
			Primary chamber			Second chamber			
Run No.	0.3% Mirex bait formulation kg/hr (lb/hr)	Contained mirex[a] g/hr	Total g/hr	Mirex conc. ppm	Total species[b] conc., ppm	Total g/hr	Mirex conc. ppm	Total species[b] conc., ppm	Ratio of total incinerator residues to total charge
A	23.95 (52.8)	72	284	4.2	51.5	60	10.8	11.6	0.016
B	23.36 (51.5)	70	267	< 0.05[c]	< 0.05	32	0.8	0.8	0.012
C	23.00 (50.7)	69	210	< 0.05[c]	0.2	37	0.2	0.6	0.011
D	10.61 (23.4)	32	170	1.6	1.8	20	0.6	0.9	0.018
E	10.80 (23.8)	32	139	0.05	< 0.3	17	0.6	1.5	0.016
F	11.02 (24.3)	33	121	0.2	3.9	21	0.5	1.6	0.013
G	11.52 (25.4)	35	80	< 0.05[c]	23.3	33	< 0.05[c]	25.6	0.010
H	23.18 (51.1)	70	197	< 0.05[c]	0.5	30	< 0.05[c]	0.7	0.010
I	22.59 (49.8)	68	231	< 0.05[c]	12.4	34	0.1	2.9	0.012
J	10.84 (23.9)	33	56	0.3	1.3	18	< 0.05[c]	1.5	0.006

Run No.	Mirex content of off-gas g/hr	Mirex content of solid residues g/hr	Mirex content of off-gas and solid residues g/hr	Total species[b] content of off-gas g/hr	Total species[b] content of solid residues g/hr	Total species[b] content of off-gas and solid residues g/hr	Ratio of mirex in off-gas to total mirex fed	Ratio of total species[b] in the off-gas to total mirex fed	Incinerator efficiency[d] % Mirex	Incinerator efficiency[d] % Total species[b]
A	7×10^{-3}	1.8×10^{-3}	9×10^{-3}	9×10^{-1}	1.4×10^{-2}	9×10^{-1}	1.0×10^{-4}	1.3×10^{-2}	> 99.98	> 98.70
B	2.4×10^{-2}	2.6×10^{-5}	2.4×10^{-2}	3.7×10^{-2}	5×10^{-5}	3.7×10^{-2}	3.4×10^{-4}	5×10^{-4}	> 99.96	> 99.94
C	2.6×10^{-2}	7×10^{-6}	2.6×10^{-2}	6×10^{-2}	6×10^{-5}	6×10^{-2}	3.5×10^{-4}	8×10^{-4}	> 99.96	> 99.91
D	6×10^{-1}	2.8×10^{-4}	6×10^{-1}	7×10^{-1}	3.2×10^{-4}	7×10^{-1}	1.8×10^{-2}	2.2×10^{-2}	> 98.21	> 97.78
E	9×10^{-2}	2.4×10^{-5}	9×10^{-2}	1.6×10^{-1}	7×10^{-5}	1.6×10^{-1}	2.9×10^{-3}	5×10^{-3}	> 99.70	> 99.50
F	2.7×10^{-2}	6×10^{-5}	2.7×10^{-2}	8×10^{-2}	5×10^{-4}	8×10^{-2}	8×10^{-4}	2.4×10^{-3}	> 99.91	> 99.75
G	4.3×10^{-2}	$< 6 \times 10^{-6}$[c]	4.3×10^{-2}	1.1×10^{-1}	$< 2.7 \times 10^{-3}$	1.1×10^{-1}	1.2×10^{-3}	3.1×10^{-3}	> 99.87	> 99.68
H	1×10^{-2}	$< 1.1 \times 10^{-5}$[c]	1×10^{-2}	3.5×10^{-2}	$< 1.2 \times 10^{-4}$	3.5×10^{-2}	1.4×10^{-4}	5×10^{-4}	> 99.98	> 99.95
I	8×10^{-2}	3.6×10^{-6}	8×10^{-2}	9×10^{-2}	3.0×10^{-3}	1×10^{-1}	1.2×10^{-3}	1.4×10^{-3}	> 99.88	> 99.85
J	8×10^{-3}	1.7×10^{-5}	8×10^{-3}	1.3×10^{-2}	1.0×10^{-4}	1.3×10^{-2}	2.3×10^{-4}	3.9×10^{-4}	> 99.97	> 99.96

---

a/ Analysis of grab samples of the bait formulation showed mirex content ranging from 0.21 to 0.41%. Because of the difficulty in obtaining representative samples of the material burned during each test (i.e., ~ 45.4 kg (100 lb) of a rather heterogeneous mixture), the nominal value of 0.3% mirex was used to calculate the quantity of contained mirex.

b/ Mirex plus all other chlorinated organic species detected.

c/ Mirex was not detected. The value given represents the detection limit for mirex in the particulate sample.

d/ Efficiency is defined as $\left[1 - \frac{\text{quantity out}}{\text{quantity in}}\right] \times 100$, where the quantity out is evaluated at Sample Points Nos. ② (incinerator off-gas) and ③ (incinerator residues), and the quantity in is evaluated at Sample Point No. ① (the incinerator feed). Efficiencies have been calculated based on (a) mirex only, and (b) the total chlorinated organic species detected at Sample Points Nos. ② and ③.

Table 89. OFF-GAS COMPOSITION--0.3% MIREX BAIT EXPERIMENTS[a]

					Total hydrocarbons analyzer			Orsat analyzer			
Run No.	Mirex mg/m^3	Total species[b] mg/m^3	SO_2 mg/m^3	NO_x[c] mg/m^3	Total hydrocarbons ppm	CO ppm	CH_4 ppm	O_2 vol. %	CO_2 vol. %	CO vol. %	Moisture vol. %
A	2.8×10^{-2}	3.5	76	13	76	65	< 1	7.8	11.4	0.0	11.6
B	8.0×10^{-2}	1.2×10^{-1}	76	39	31	ND[d]	< 1	9.7	9.6	0.0	7.2
C	6.3×10^{-2}	1.5×10^{-1}	87	32	63	ND	< 1	9.6	9.6	0.0	5.3
D	1.9	2.4	44	59	93	63	< 1	14.6	5.2	0.0	7.9
E	5.8×10^{-1}	9.9×10^{-1}	119	26	55	5	< 1	9.4	9.6	0.0	5.0
F	1.6×10^{-1}	4.8×10^{-1}	199	43	24	20	< 1	7.0	11.4	0.0	3.0
G	1.1×10^{-1}	2.8×10^{-1}	129	52	29	4	< 1	11.6	7.6	0.0	7.0
H	2.1×10^{-2}	7.7×10^{-2}	71	52	31	ND	< 1	11.7	7.9	0.0	7.4
I	2.0×10^{-1}	2.4×10^{-1}	50	54	33	26	< 1	12.6	7.2	0.0	7.5
J	1.8×10^{-2}	3.0×10^{-2}	131	55	20	ND	< 1	12.5	6.8	0.0	7.3

---

[a] As dry gas at one atmosphere pressure, and 21.1°C (70°F).
[b] Mirex plus all other chlorinated organic species detected.
[c] Calculated as NO_2.
[d] Not detected.

Table 90. OPERATIONAL DATA SUMMARY--0.3% MIREX BAIT EXPERIMENTS

Run No.	A	B	C	D	E	F	G
Temperature °C (°F)							
Primary chamber (Thermocouple No. ①)	850 (1570)	820 (1510)	880 (1610)	570 (1050)	700 (1290)	810 (1490)	890 (1640)
Primary chamber (Thermocouple No. ②)	970 (1780)	940 (1720)	1050 (1930)	690 (1270)	720 (1320)	790 (1460)	950 (1750)
Primary chamber (Thermocouple No. ③)	900 (1650)	870 (1600)	930 (1710)	590 (1090)	690 (1280)	820 (1510)	940 (1730)
Second chamber (Thermocouple No. ④)	700 (1300)	670 (1230)	780 (1440)	510 (950)	570 (1060)	680 (1250)	830 (1520)
Second chamber (Thermocouple No. ⑤)	500 (930)	490 (920)	620 (1150)	390 (730)	390 (730)	440 (830)	650 (1210)
Sample Point No. ② (Thermocouple No. ⑥)	310 (590)	310 (590)	400 (760)	270 (510)	230 (450)	270 (520)	420 (790)
Pressures							
Draft (Manometer No. ⚠), pascals (in H_2O) gauge	36 (0.145)	54 (0.215)	62 (0.250)	42 (0.170)	17 (0.070)	19 (0.075)	62 (0.250)
Burner operation pressure, pascals (psi) gauge	7.4×10^5 (108)	7.5×10^5 (109)	7.4×10^5 (108)	7.6×10^5 (110)	7.4×10^5 (108)	7.4×10^5 (108)	7.4×10^5 (108)
Pesticide injection air, pascals (psi) gauge	8×10^4 (11)	7×10^4 (10)	8×10^4 (12)	8×10^4 (12)	6×10^4 (9)	6×10^4 (9)	6×10^4 (9)
Scrubber liquids[a]							
1st Stage, H_2O scrubber							
Volume, ℓ (gal.)	1110 (293)	1070 (282)	1100 (291)	1260 (334)	1020 (270)	1033 (273)	1030 (271)
Mirex conc., mg/ℓ	1×10^{-1}	1	6×10^{-2}	7×10^{-1}	6×10^{-2}	2×10^{-2}	NA[d]
Total species conc.,[b] mg/ℓ	5×10^{-1}	2	8×10^{-2}	7×10^{-1}	7×10^{-2}	2×10^{-2}	NA[d]
2nd Stage, hexalene glycol scrubber							
Volume, ℓ (gal.)	100 (26.3)	99 (26.1)	101 (26.8)	96 (25.4)	94 (24.8)	93 (24.6)	96 (25.4)
Mirex conc. change, mg/ℓ	ND[c]	NA[d]	7×10^{-2}	9×10^{-1}	ND[c]	4×10^{-1}	1
Total species conc. change,[b] mg/ℓ	ND	NA	1×10^{-1}	2	ND	1	7
3rd Stage, H_2O scrubber							
Volume, ℓ (gal.)	2030 (537)	2010 (531)	1950 (514)	1020 (269)	1820 (480)	1840 (486)	1820 (480)
Mirex conc., mg/ℓ	2×10^{-3}	3×10^{-2}	6×10^{-3}	NA[d]	9×10^{-3}	NA[d]	2×10^{-3}
Total species conc.,[b] mg/ℓ	5×10^{-2}	3×10^{-2}	8×10^{-3}	NA	1×10^{-2}	NA	8×10^{-3}
Scrubber system							
Effluent gas (Sample Point No. ⑨)[e]							
Mirex conc., mg/m^3	6×10^{-3}	1×10^{-2}	2×10^{-3}	2×10^{-1}	9×10^{-3}	6×10^{-3}	3×10^{-3}
Total species conc.,[b] mg/m^3	2×10^{-1}	2×10^{-2}	3×10^{-3}	2×10^{-1}	7×10^{-2}	3×10^{-2}	7×10^{-3}

Table 90. (Concluded)

Run No.	H	I	J
Temperature °C (°F)			
Primary chamber (Thermocouple No. ①)	830 (1530)	720 (1330)	890 (1630)
Primary chamber (Thermocouple No. ②)	980 (1800)	890 (1630)	960 (1760)
Primary chamber (Thermocouple No. ③)	880 (1620)	760 (1400)	920 (1690)
Second chamber (Thermocouple No. ④)	790 (1450)	630 (1160)	840 (1540)
Second chamber (Thermocouple No. ⑤)	650 (1200)	520 (960)	680 (1260)
Sample Point No. ⑦ (Thermocouple No. ⑥)	430 (800)	360 (640)	450 (850)
Pressures			
Draft (Manometer No. △1), pascals (in H_2O) gauge	60 (0.240)	51 (0.205)	57 (0.230)
Burner operation pressure, pascals (psi) gauge	7.6 × 10^5 (110)	7.4 × 10^5 (108)	7.4 × 10^5 (108)
Pesticide injection air, pascals (psi) gauge	8 × 10^4 (12)	8 × 10^4 (12)	8 × 10^4 (12)
Scrubber liquids[a/]			
1st Stage, H_2O scrubber			
Volume, ℓ (gal.)	1160 (306)	1040 (275)	1020 (270)
Mirex conc., mg/ℓ	1 × 10^{-2}	7 × 10^{-2}	2 × 10^{-2}
Total species conc.,[b/] mg/ℓ	2 × 10^{-2}	1 × 10^{-1}	4 × 10^{-4}
2nd Stage, hexylene glycol scrubber			
Volume, ℓ (gal.)	97 (25.6)	94 (24.8)	96 (25.3)
Mirex conc. change, mg/ℓ	2 × 10^{-1}	2	NI[c/]
Total species conc. change,[b/] mg/ℓ	2	5	9 × 10^{-1}
3rd Stage, H_2O scrubber			
Volume, ℓ (gal.)	1930 (509)	1730 (457)	1790 (474)
Mirex conc., mg/ℓ	2 × 10^{-3}	1 × 10^{-3}	1 × 10^{-3}
Total species conc.,[b/] mg/ℓ	6 × 10^{-3}	2 × 10^{-2}	2 × 10^{-2}
Scrubber system			
Effluent gas (Sample Point No. ⑨)[e/]			
Mirex conc., mg/m^3	< 4 × 10^{-3}[f/]	< 4 × 10^{-3}[f/]	5 × 10^{-3}
Total species conc.,[b/] mg/m^3	7 × 10^{-3}	3.5 × 10^{-1}	9 × 10^{-2}

[a/] Scrubber water (Scrubbers 1 and 3) was used once through, while the hexylene glycol (Scrubber 2) was recycled. The concentrations reported for hexylene glycol, therefore, are the concentration changes (increases) detected during the respective tests.

[b/] Mirex plus all other chlorinated organic species detected.

[c/] No increase in concentration detected.

[d/] No analysis.

[e/] As the wet gas at one atmosphere pressure, and 21.1°C (70°F).

[f/] Mirex not detected. The value reported represents the limit of detection for this particular sample.

Table 91. PARTICULATE SAMPLING SUMMARY--0.3% MIREX BAIT EXPERIMENTS

Description	A	B	C	D	E	F	G	H	I	J
Vol. dry gas - std. cond., nm^3	0.429	0.537	0.650	0.501	0.279	0.258	0.592	0.707	0.674	0.731
Percent moisture by vol.	11.6	7.2	5.3	7.9	5.0	3.0	7.0	7.4	7.5	7.3
Avg. stack temperature, °C	307.2	296.1	402.6	256.7	242.4	305.3	476.4	432.9	364.1	468.7
Stk. flow rate, dry, std. cond., nm^3/min	4.4	5.0	6.4	5.0	2.7	2.8	6.5	7.6	6.5	7.1
Actual stack flow rate, m^3/min	9.8	10.6	15.5	9.7	4.9	5.5	17.7	19.6	15.4	19.6
Percent isokinetic	93.6	102.3	97.4	96.5	99.3	88.6	87.2	88.7	98.5	98.4
Percent excess air	58	86	82	229	80	48	57	123	150	142
Particulates - partial catch										
Particulate wt. - partial, mg	86	64	73	69	23	31	45	78	58	51
Part. load - ptl., std. cn., mg/nm^3	195	119	112	138	82	120	77	111	86	70
Part. load - ptl., stk. cn., mg/m^3	89	56	46	70	45	60	28	43	36	25
Partic. emis. - partial, kg/hr	0.052	0.036	0.043	0.041	0.013	0.020	0.030	0.051	0.034	0.030
Particulates - total catch										
Particulate wt. - total, mg	174	95	111	124	46	62	63	84	72	62
Part. load - ttl., std. cn., mg/nm^3	405	177	171	246	164	238	106	118	107	85
Part. load - ttl., std. cn., corrected to 12% CO_2, mg/nm^3	426	222	213	570	205	251	168	180	179	130
Part. load - ttl., stk. cn., mg/m^3	182	84	70	126	90	118	39	46	46	31
Partic. emis. - total, kg/hr	0.106	0.053	0.065	0.073	0.027	0.040	0.041	0.054	0.042	0.036
Percent impinger catch	50.78	33.00	34.13	43.86	49.85	49.76	28.04	6.55	20.09	17.86

Additional samples were taken during the mirex tests using a special sampler installed in the bottom of the primary combustion chamber (see Figure 32, p.196). This sampler was used to catch the mirex bait particles as they fell through the combustion chamber in order to approximate the degree of decomposition actually occurring while the particle was falling. The sampler was inserted upside down, rotated, and immediately (≈ 3 sec) extracted to obtain grab samples with a nominal retention time in the primary combustion chamber of about 2 sec. The grab samples were analyzed for mirex and total chlorinated species content and gave the following results:

Grab Sample Composition

Run No.	Mirex (ppm)	Total Species (ppm)[a]
A	170	220
B	960	960
C	460	460
D	2,090	2,090
E	1,000	1,000
F	700	1,190
G	270	310
	200	300
H	1,220	1,220
	220	220
I	200	400
	1,190	1,460
J	1,750	1,770
	400	1,020
Average	770	900

---

[a] Mirex plus all other chlorinated organic species detected.

The average mirex content of the bait formulation used for these tests was 2,710 ppm (based on 17 samples, ranging from 1,940 to 4,130 ppm). Although the above data show no strong correlation with any particular operating parameter, they do indicate that a substantial portion of the mirex (~ 70%) is "removed" from the bait formulation during the first 2 sec residence in the primary chamber.

The data do not show what operating conditions would be required to effect mirex decomposition comparable to that which has been achieved for the other pesticides studied (i.e., an incineration efficiency of > 99.99%). It appears that temperatures higher than those tested (above 940°C (1730°F)) both will be required.

The results from particulate sampling of the mirex test are summarized in Table 91.* Seven of the 10 runs were within acceptable isokinetic limits (100 ± 10%). Runs Nos. F, G, and H, although not acceptable, were close enough to being isokinetic as to provide valuable information. Four of the runs (G, H, I, and J) had particulate emissions rates within established incinerator limits.

DISCUSSION

There were no specific operational problems with mirex. As was noted above, however, the fact that the mirex bait was formulated on a combustible inert carrier resulted in the continued burning of the solid residue in the bottom of the primary combustion chamber throughout the experiments.

---

* Initial analysis of the particulate emission samples showed an unreasonably high particulate catch in the liquid nitrogen cold trap for Runs Nos. E, F, G, and H, equal to 90 to 98% of the apparent total particulate emission. These values were not included in the values reported in Table 91.

References

1. Martin, H., Pesticide Manual, 2nd Edition, British Crop Protection Council, Worcester, England (1971).

2. Lawless, E. W., T. L. Ferguson, and A. F. Meiners, "Guidelines for the Disposal of Small Quantities of Unused Pesticides," (Draft), EPA Contract No. 68-01-0098 (1974).

APPENDIX C

SAMPLING AND ANALYSIS

CONTENTS

Page

I. Active Ingredient and Related Chemical Compounds. 336

- Incinerator Feed. 336
- Incinerator Effluent - Liquid Pesticide Formulations. . 336
- Incinerator Effluent - Solid Pesticide Formulations . . 341
- Scrubbed Gas. 354
- Scrubber Liquids. 357
- Solid Residues. 358

II. Other Sampling and Analysis 362

- Sulfur Dioxide. 362
- Nitrogen Oxides 367
- Moisture. 373
- Excess Air. 378
- Total Hydrocarbons. 380

III. Special Analysis. 382

- Cyanide 382
- Total Phrophosphates. 386

I. ACTIVE INGREDIENT AND RELATED CHEMICAL COMPOUNDS

A. INCINERATOR FEED

1. Liquid Formulations

a. Samples of the liquid formulation were collected through a valve on the burner between the pump and the nozzle.

b. The method of sample collection consisted of the following:

(1) Purge the sample valve and line with approximately 75 ml of the liquid formulation mix.

(2) Fill the sample bottle.

(3) Purging the sample line and collecting the sample should be done slowly so that the flow to the nozzle is not affected.

2. Solid Formulations

a. Solid formulation samples were collected from the delivery spout of the vibrating screw feeder before the test and at the conclusion of the test.

b. The samples were weighed and the net weight subtracted from the weight of the charge.

B. INCINERATOR EFFLUENT - LIQUID PESTICIDE FORMULATIONS

1. Apparatus (see Figure 64)

a. Sampling

(1) Probe - Pyrex® glass probe 7 mm I.D. and of sufficient length for the inlet to be at midstream (centroid) of the stack.

(2) Midget impingers - Three.

(3) Filters and casing - Millepore, Type AA, 0.8 μ opening with a fiberglass filter for support.

(4) Critical orifice - 26G-3/8 in. needle allowing a flow rate of about 0.3 liters/min.

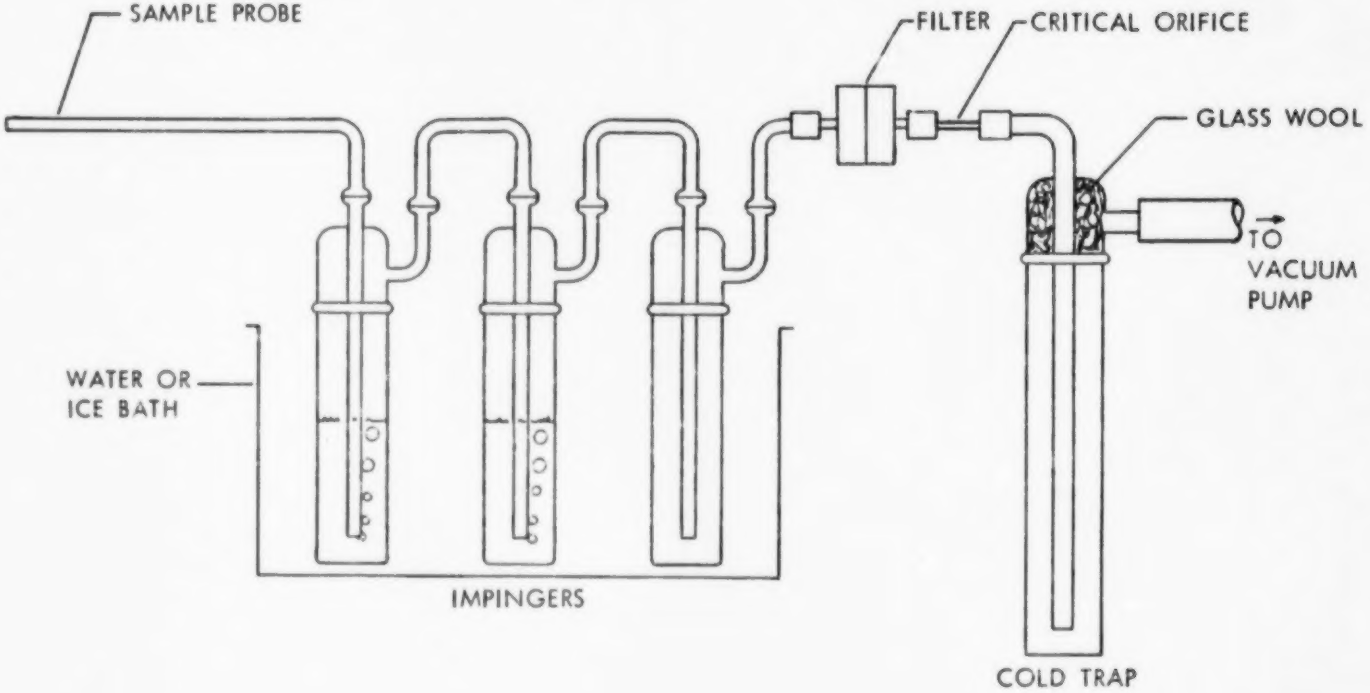


Figure 64. Gas sampling train

(5) Cold trap.

(6) Vacuum pump - To pull stack gas through the train.

(7) Rotometer - For checking the dry gas flow rate through the sampling train, 0 to 0.5 liter/min.

(8) Dewer flask - 1-qt capacity.

(9) Glass wool.

(10) Automatic pipette - Delivery capacity of 20 ml.

(11) Septum - 7 mm.

b. Sample Recovery

(1) Glass wash bottles - Two.

(2) Sample containers - 1-oz French Squares, and one 3-oz bottle.

2. Reagents

a. Solvent - Pesticide grade as appropriate to the pesticide being tested, see Table 92.

b. Water - Distilled deionized.

c. Acetone - Reagent grade.

d. Chromic acid - 160 ml concentrated sulfuric acid added to 100 ml saturated potassium dichromate.

e. Liquid nitrogen.

3. Procedure

a. Wash procedure - For sample bottles and caps, probe, impingers, filter casing and cold trap.

(1) Detergent and water.

(2) Rinse twice in tap water.

(3) Chromic acid rinse.

(4) Deionized, distilled water rinse twice.

(5) Acetone rinse - Except filter casings.

(6) Oven dry - 110°C.

Table 92. SOLVENT SELECTION

Pesticide	First impinger	Second impinger
DDT	Benzene	Benzene
Aldrin	2,2,4-Trimethylpentane	2,2,4-Dimethylpentane
Picloram	Distilled, deionized water	2-Propanol
Malathion	Benzene	pH 4 Sulfuric acid
Toxaphene	2,2,4-Trimethylpentane	2,2,4-Trimethylpentane
Atrazine	Benzene	2-Propanol
Captan	Benzene	Benzene
Zineb	Distilled, deionized water	Distilled, deionized water
Mirex	Benzene	Benzene

b. Train Preparation

(1) Pipette 20 ml of solvent into each of two impingers.

(2) Transfer a fiberglass filter and a Type AA Millepore filter to the casing with clean tongs. Assemble the filter casing and tape closed.

(3) Assemble the cold trap.

(4) Assemble the train as shown in Figure 64.

(5) Tape the probe and the cold trap closed with masking tape to prevent contamination during transport and installation.

c. Sampling

(1) Install the train at Sampling Point No. ② with the inlet of the sample probe at midstream.

(2) Check the gas flow rate with a rotometer. The probe should be temporarily disconnected.

(3) Sample the stack gas 30 min.

(4) Again check the gas flow rate, as above, at the end of the experimental test.

d. Sample Recovery

(1) Transfer the contents of the impingers into separate sample bottles.

(2) Tape the cold trap closed for shipment intact.

(3) Tape the filter casing closed for shipment intact.

(4) Rinse the probe, the impingers and the connecting glassware with the solvent of the test and transfer the rinsings to the 3-oz sample bottle.

(5) Send as blanks, samples of solvent, acetone and deionized, distilled water in separate bottles.

(6) Send as a blank an assembled filter and casing taped closed.

C. INCINERATOR EFFLUENT - SOLID PESTICIDE FORMULATIONS

1. Principle

Particulate matter is withdrawn isokinetically from the source and its weight is determined gravimetrically after removal of uncombined water.

2. Apparatus

a. Sampling train - The design specifications of the particulate sampling train used by EPA (Figure 65) are described in APTD-0581. Commercial models of this train are available.

(1) Nozzle - Stainless steel (316) with sharp, tapered leading edge.

(2) Probe - Pyrex® glass 3 ft in length, with a heating system capable of maintaining a minimum gas temperature of 250°F at the exit end during sampling to prevent condensation from occurring.

(3) Pitot tube - Type S attached to probe to monitor stack gas velocity.

(4) Filter holder - Pyrex® glass with heating system capable of maintaining minimum temperature of 225°F.

(5) Impingers/condenser - Five impingers connected in series with glass ball joint fittings. The first, third, fourth, and fifth impingers are of the Greenburg-Smith design, modified by replacing the tip with a 1/2-in. I.D. glass tube extending to 1/2-in. from the bottom of the flask. The second impinger is of the Greenburg-Smith design with the standard tip.

(6) Metering system - Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 5°F, dry gas meter with 2% accuracy, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume.

(7) Barometer - To measure atmospheric pressure to ± 0.1 in. Hg.

(8) Dewar flask - Four liters capacity.

(9) 125 ml cyclone flask - One.

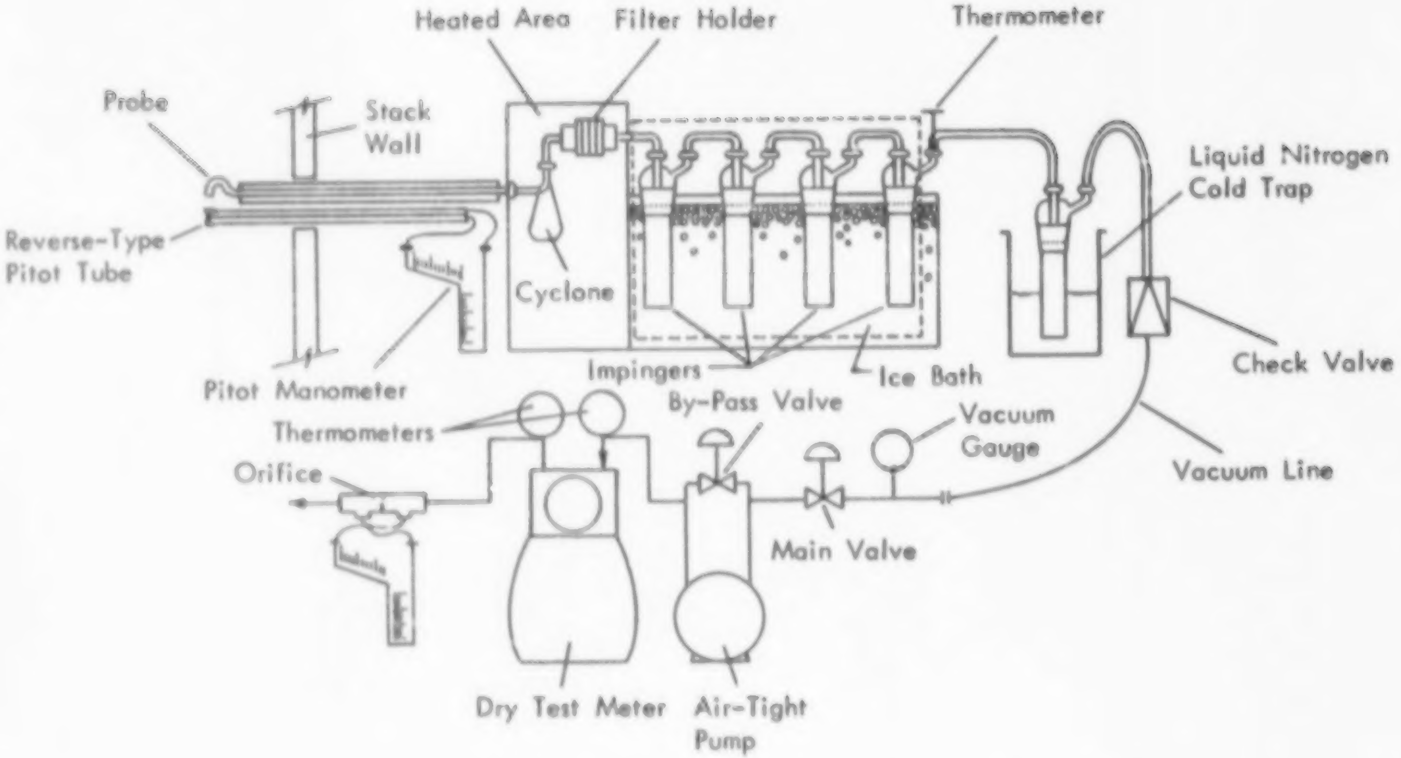


Figure 65. Particulate-sampling train

b. Sample Recovery

(1) Probe brush - At least as long as probe.

(2) Glass wash bottles - Two.

(3) Glass sample storage containers.

(4) Graduated cylinder - 250 ml.

c. Analysis

(1) Glass weighing dishes.

(2) Desiccator.

(3) Analytical balance - To measure to ± 0.1 mg.

(4) Trip balance - 300 g capacity, to measure to ± 0.05 g.

3. Reagents

a. Sampling

(1) Filters - Glass fiber, MSA 1106 BH, or equivalent, numbered for identification and preweighed.

(2) Silica gel - Indicating type, 6 to 16 mesh, dried at 175°C (350°F) for 2 hr.

(3) Water.

(4) Crushed ice.

(5) Appropriate solvent(s). (See Table 92.)

(6) Liquid nitrogen.

b. Sample Recovery

(1) Acetone - Reagent grade.

c. Analysis

(1) Water.

(2) Desiccant - Drierite®, indicating.

4. Procedure

a. Sampling

(1) Preparation of collection train - Weight to the nearest gram approximately 200 g of silica gel. Label a filter of proper diameter, desiccate* for at least 24 hr and weigh to the nearest 0.5 mg in a room where the relative humidity is less than 50%. Place 100 ml of solvent in each of the first two impingers, leave the third impinger empty, and place approximately 200 g of preweighed silica gel in the fourth impinger. Set up the train without the probe as in Figure 65. Leak check the sampling train at the sampling site by plugging up the inlet to the filter holder and pulling a 15-in. Hg vacuum. A leakage rate not in excess of 0.02 cfm at a vacuum of 15 in. Hg is acceptable. Attach the probe and adjust the heater to provide a gas temperature of about 250°F, at the probe outlet. Turn on the filter heating system. Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger as low as possible and preferably at 70°F, or less. Temperatures above 70°F may result in damage to the dry gas meter from either moisture condensation or excessive heat.

(2) Determine the stack pressure, temperature, moisture, and range of velocity head.

(3) Particulate train operation - For each run, record the data required on the example sheet shown in Figure 66. Take readings at each sampling point every 5 min, and when significant changes in stack conditions necessitate additional adjustments in flow rate. To begin sampling, position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Sample for 5 min at each of the 12 traverse points; sampling time must be the same for each point. Maintain isokinetic sampling throughout the sampling period. Nomographs are available which aid in the rapid adjustment of the sampling rate without other computations. APTD-0576 details the procedure for using these nomographs. Turn off the pump at the conclusion of each run and record the final readings. Remove the probe and nozzle from the stack and handle in accordance with the sample recovery process described in Section 4-b.

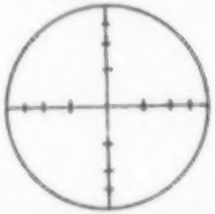
b. Sample recovery - Exercise care in moving the collection train from the test site to the sample recovery area to minimize the loss of collected sample or the gain of extraneous particulate matter. Set aside a portion of the acetone used in the sample recovery as a blank for analysis. Measure the volume of water from the first three impingers. Place the samples in containers as follows:

---

* Dry using Drierite® at 70°F ± 10°F.

FIELD DATA

PLANT ______
DATE ______
SAMPLING LOCATION ______
SAMPLE TYPE ______
RUN NUMBER ______
OPERATOR ______
AMBIENT TEMPERATURE ______
BAROMETRIC PRESSURE ______
STATIC PRESSURE, (P_s) ______
FILTER NUMBER (s) ______



SCHEMATIC OF TRAVERSE POINT LAYOUT

PROBE LENGTH AND TYPE ______
NOZZLE I.D. ______
ASSUMED MOISTURE, % ______
SAMPLE BOX NUMBER ______
METER BOX NUMBER ______
METER $\Delta H_@$ ______
C FACTOR ______
PROBE HEATER SETTING ______
HEATER BOX SETTING ______
REFERENCE Δp ______

READ AND RECORD ALL DATA EVERY ______ MINUTES

TRAVERSE POINT NUMBER	SAMPLING TIME, min / CLOCK TIME (24-hr CLOCK)	GAS METER READING (V_m), ft^3	VELOCITY HEAD (Δp_s), in. H_2O	ORIFICE PRESSURE DIFFERENTIAL (ΔH), in. H_2O		STACK TEMPERATURE (T_s), °F	DRY GAS METER TEMPERATURE		PUMP VACUUM, in. Hg	SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
				DESIRED	ACTUAL		INLET $(T_{m_{in}})$, °F	OUTLET $(T_{m_{out}})$, °F			

COMMENTS

EPA (Dur) 235
4 72

Figure 66. Particulate field data

Container No. 1 - Remove the filter from its holder, place in this container, and seal.

Container No. 2 - Place loose particulate matter and acetone washings from all sample-exposed surfaces prior to the filter in this container and seal. Use a razor blade, brush, or rubber policeman to loosen adhering particles.

Container No. 3 - Measure the volume of water in Impinger No. 1, and record. Transfer the contents of Impinger No. 1 and a solvent rinse into Container No. 3.

Container No. 4 - Measure the volume of water in Impinger No. 2 and record. Transfer the contents and a solvent rinse into Container No. 4.

Container No. 5 - Measure the volume of water in Impinger No. 3 and record. Transfer the contents of Impinger No. 3 and a solvent rinse into Container No. 5.

Container No. 6 - Weigh and transfer the silica gel from the fourth impinger to Container No. 6 and seal. Use a rubber policeman as an aid in removing silica gel from the impinger.

Container No. 7 - Rinse all four impingers and all connecting glass after the filter and before Impinger No. 4 with solvent. Transfer the above into Container No. 7.

Container No. 8 - Transfer the contents of the cold trap and a solvent rinse into Container No. 8.

Container No. 9 - Rinse Impingers 1, 2, 3, 4, the cold trap and all connecting glass after the filter and before the cold trap with acetone. Transfer into Container No. 9.

Container No. 10 - Solvent blank.

Container No. 11 - Acetone blank.

c. Analysis - Record the data required on the example sheet shown in Figure 66. Handle each sample container as follows:

Container No. 1 - Transfer the filter and any loose particulate matter from the sample container to a tared glass weighing dish, desiccate, and dry to a constant weight. Report results to the nearest 0.5 mg.

Container No. 2 - Transfer the acetone washings to a tared beaker and evaporate to dryness at ambient temperature and pressure. Desiccate and dry to a constant weight. Report results to the nearest 0.5 mg.

Containers Nos. 3, 4, 5, 7, 8, 9 - Transfer the contents of each of the Containers Nos. 3, 4, 5, 7, 8, 9 into separate tared beakers. Evaporate to dryness at ambient temperature and pressure. Desiccate and dry to a constant weight. Weigh and report results to the nearest 0.5 mg.

5. Calibration

Use methods and equipment which have been approved to calibrate the orifice meter, pitot tube, dry gas meter, and probe heater. Recalibrate after each test series.

6. Calculations

a. Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 66).

b. Dry Gas Volume - Correct the sample volume measured by the dry gas meter to standard conditions 70°F, 29.92 in. Hg) by using Eq. C-1.

$$V_{m_{std}} = V_m \left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar} + \dfrac{\Delta H}{13.6}}{P_{std}}\right) = \left(17.71 \frac{°R}{\text{in. Hg}}\right) V_m \left(\frac{P_{bar} + \dfrac{\Delta H}{13.6}}{T_m}\right) \quad \text{(C-1)}$$

where $V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions) cubic feet

V_m = Volume of gas sample through the dry gas meter (meter conditions) cubic feet

T_{std} = Absolute temperature at standard conditions, 530°R

T_m = Average dry gas meter temperature, °R

P_{bar} = Barometric pressure at the orifice meter, inches Hg

ΔH = Average pressure drop across the orifice meter, inches H_2O

13.6 = Specific gravity of Hg.

P_{std} = Absolute pressure at standard conditions, 29.92 in. Hg.

c. Volume of Water Vapor

$$V_{w_{std}} = V_{1_o} \left(\frac{\rho H_2O}{M_{H_2O}}\right) \left(\frac{RT_{std}}{P_{std}}\right) = \left(0.0474 \ \frac{\text{cu ft}}{\text{ml}}\right) V_{1_o} \qquad \text{(C-2)}$$

where $V_{w_{std}}$ = Volume of water vapor in the gas sample (standard conditions), cubic feet

V_{1_o} = Total volume of liquid collected in impingers and silica gel (see Figure 67), milliliters

ρH_2O = Density of water, 1 g/ml

M_{H_2O} = Molecular weight of water, 18 lb/lb-mole

R = Ideal gas constant, 21.83 in. Hg--cubic feet/pound--mole °R

T_{std} = Absolute temperature at standard conditions, 530°R

P_{std} = Absolute pressure at standard conditions, 29.92 in. Hg

d. Moisture Content

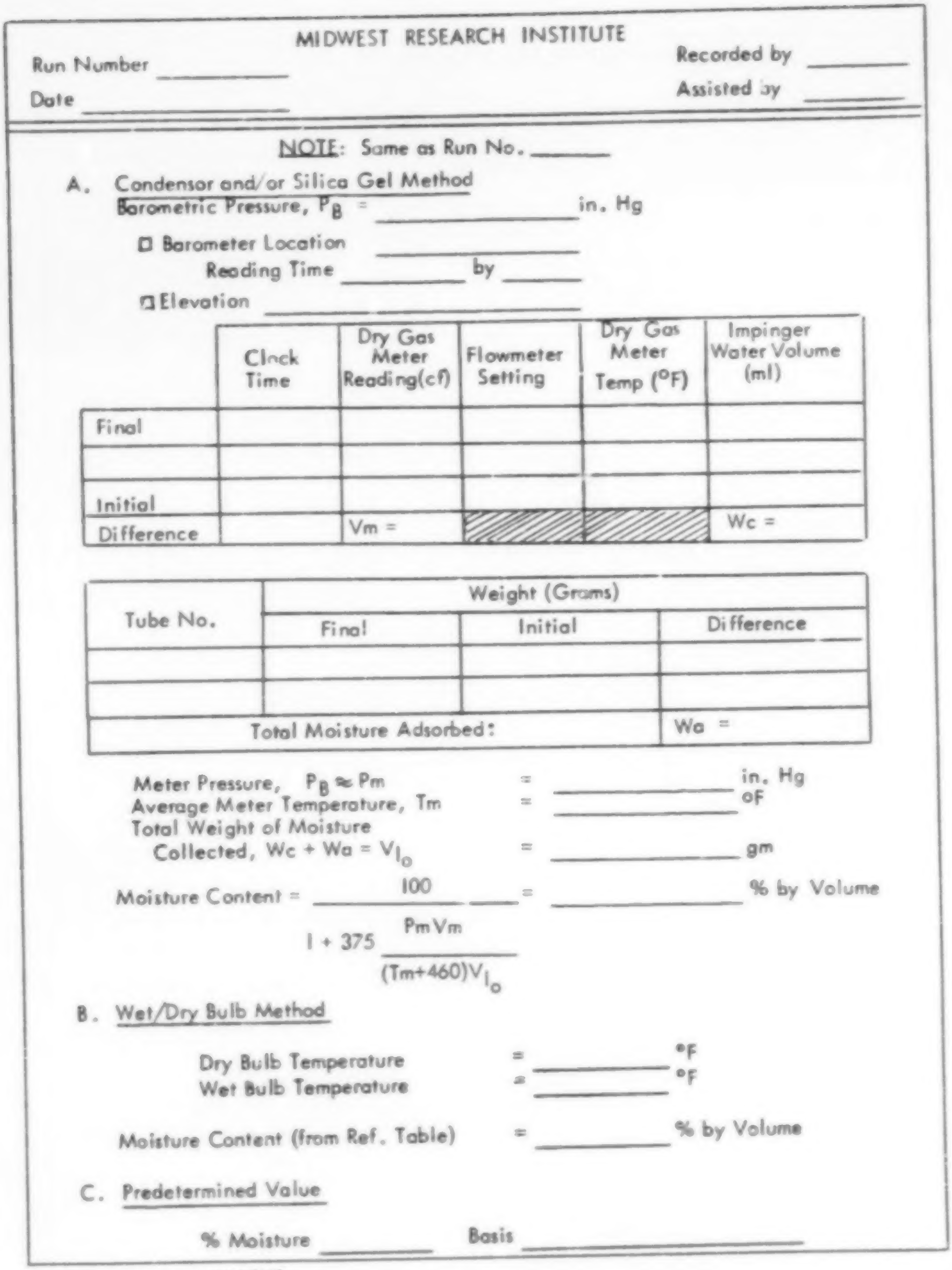
$$B_{wo} = \frac{V_{w_{std}}}{V_{m_{std}} + V_{w_{std}}} \qquad \text{(C-3)}$$

where B_{wo} = Proportion by volume of water vapor in the gas stream, dimensionless.

$V_{w_{std}}$ = Volume of water in the gas sample (standard conditions), cubic feet.

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cubic feet

e. Partial particulate weight (M_{np}) - Determine the partial particulate catch from the sum of the weights of Containers Nos. 1 and 2 on the analysis data sheet (Figure 68).



MIDWEST RESEARCH INSTITUTE

Run Number __________

Date ______________

Recorded by ________

Assisted by ________

NOTE: Same as Run No. ______

A. Condensor and/or Silica Gel Method

Barometric Pressure, P_B = ______________ in. Hg

☐ Barometer Location ______________

Reading Time __________ by ______

☐ Elevation ______________

	Clock Time	Dry Gas Meter Reading (cf)	Flowmeter Setting	Dry Gas Meter Temp (°F)	Impinger Water Volume (ml)
Final					
Initial					
Difference		Vm =	▨	▨	Wc =

Tube No.	Weight (Grams)		
	Final	Initial	Difference
Total Moisture Adsorbed:			Wa =

Meter Pressure, $P_B \approx P_m$ = ______________ in. Hg

Average Meter Temperature, Tm = ______________ °F

Total Weight of Moisture Collected, $W_c + W_a = V_{l_o}$ = ______________ gm

$$\text{Moisture Content} = \cfrac{100}{1 + 375\,\cfrac{P_m V_m}{(T_m+460)V_{l_o}}} = \text{\_\_\_\_\_\_\_\_\_\_ \% by Volume}$$

B. Wet/Dry Bulb Method

Dry Bulb Temperature = __________ °F

Wet Bulb Temperature = __________ °F

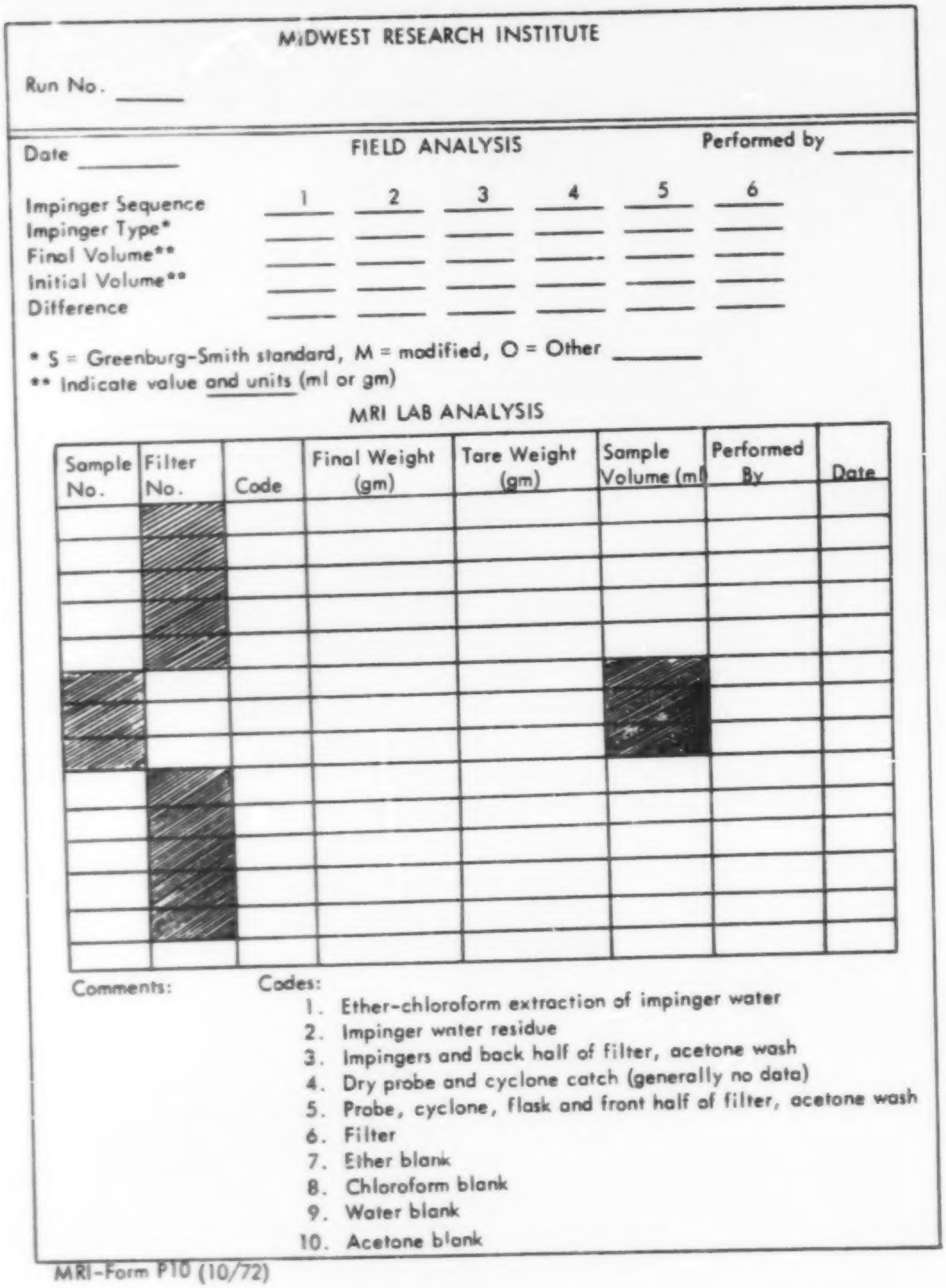
Moisture Content (from Ref. Table) = __________ % by Volume

C. Predetermined Value

% Moisture __________ Basis ______________

MRI - Form P4 (10/72)

Figure 67. Preliminary moisture determination data



MIDWEST RESEARCH INSTITUTE

Run No. ______

Date ________ FIELD ANALYSIS Performed by ______

Impinger Sequence	1	2	3	4	5	6
Impinger Type*						
Final Volume**						
Initial Volume**						
Difference						

* S = Greenburg-Smith standard, M = modified, O = Other ______

** Indicate value and units (ml or gm)

MRI LAB ANALYSIS

Sample No.	Filter No.	Code	Final Weight (gm)	Tare Weight (gm)	Sample Volume (ml)	Performed By	Date
	▨						
	▨						
	▨						
	▨						
	▨						
▨					▨		
▨					▨		
▨					▨		
	▨						
	▨						
	▨						
	▨						
	▨						

Comments:

Codes:

1. Ether-chloroform extraction of impinger water
2. Impinger water residue
3. Impingers and back half of filter, acetone wash
4. Dry probe and cyclone catch (generally no data)
5. Probe, cyclone, flask and front half of filter, acetone wash
6. Filter
7. Ether blank
8. Chloroform blank
9. Water blank
10. Acetone blank

MRI-Form P10 (10/72)

Figure 68. Particulate clean-up and analysis data

f. Total particulate weight (M_{NT}) - Determine the total particulate catch from the sum of the weights of container Nos. 1-5, 7-9 on the analysis data sheet (Figure 68).

g. Concentration

(1) Concentration in grains/standard cubic foot, partial.

$$C_s'' = \left(0.0154 \frac{gr}{mg}\right)\left(\frac{M_{np}}{V_{m_{std}}}\right) \qquad \text{(C-4)}$$

where C_s'' = Partial concentration of particulate matter in stack gas, grains/standard cubic foot, dry basis

M_{np} = Partial amount of particulate matter collected, milligrams

$V_{m_{std}}$ = Volume of gas sample through dry gas meter (standard conditions), cubic feet

(2) Concentration in grains/standard cubic foot, total

$$C_s' = \left(0.0154 \frac{gr}{mg}\right)\left(\frac{M_{NT}}{V_{m_{std}}}\right) \qquad \text{(C-5)}$$

where C_s' = Total concentration of particulate matter in stack gas, grains/standard cubic foot, dry basis

M_{NT} = Total amount of particulate matter collected, milligrams

$V_{m_{std}}$ = Volume of gas sample through dry gas meter (standard conditions), cubic feet

(3) Concentration in pounds/standard cubic foot, total

$$C_s = \frac{\left(\frac{1}{453,600}\ \frac{lb}{mg}\right) M_{NT}}{V_{m_{std}}} = 2.205 \times 10^{-5} \frac{M_{NT}}{V_{m_{std}}} \qquad \text{(C-6)}$$

where C_s = Concentration of particulate matter in stack gas, pounds/standard cubic foot, dry basis, total

453,600 = Milligrams/pound

M_{NT} = Total amount of particulate matter collected, milligrams

$V_{m_{std}}$ = Volume of gas sample through dry gas meter (standard conditions), cubic feet

(4) Concentration normalized to 12% CO_2, grains/standard cubic foot, total.

$$C_N = \left(\frac{12}{\%\ CO_2}\right) C'_s \qquad \text{(C-7)}$$

where C_N = Concentration of particulate matter in the stack gas normalized to 12% CO_2, grains/standard cubic foot, dry basis, total

% CO_2 = Actual concentration of CO_2 in the stack gas as determined by Orsat analysis, percent

C'_s = Total concentration of particulate matter in the stack gas, grains/standard cubic foot, dry basis

h. Isokinetic Variation

$$I = \frac{T_s\left[\dfrac{V_{1_o}(\rho H_2O)R}{M_{H_2O}} + \dfrac{V_m}{T_m}\left(P_{bar} + \dfrac{\Delta H}{13.6}\right)\right]}{\theta\ V_s P_s A_n} \times 100 \qquad \text{(C-8)}$$

$$= \frac{\left(1.667\ \frac{\text{min}}{\text{sec}}\right)\left[\left(0.00267\ \frac{\text{in. Hg-cu ft}}{\text{ml-°R}}\right) V_{1_o} + \dfrac{V_m}{T_m}\left(P_{bar} + \dfrac{\Delta H}{13.6}\right)\right]}{\theta\ V_s P_s A_n}$$

where I = Percent of isokinetic sampling

V_{l_o} = Total volume of liquid collected in impingers and silica gel (see Figure 67), milliliters

ρH_2O = Density of water, 1 g/ml

R = Ideal gas constant, 21.83 in. Hg-cubic feet/pound mole, °R

M_{H_2O} = Molecular weight of water, 18 lb/lb-mole

V_m = Volume of gas sample through the dry gas meter (meter conditions), cubic feet

T_m = Absolute average dry gas meter temperature (see Figure 66), °R

P_{bar} = Barometric pressure at sampling site, inches Hg

ΔH = Average pressure drop across the orifice (see Figure 66), inches H_2O

T_s = Absolute average stack gas temperature (see Figure 66), °R

θ = Total sampling time, minutes

V_s = Stack gas velocity calculated by Eq. D-14, Appendix D, ft/sec

P_s = Absolute stack gas pressure, inches Hg

A_n = Cross-sectional area of nozzle, square feet

i. Acceptable Results - The following range sets the limit on acceptable isokinetic sampling results:

If $90\% \le I \le 110\%$, the results are acceptable; otherwise, reject the results and repeat the test.

Adapted from Federal Register, Vol. 36, No. 247, Thursday, 23 December 1971.

D. SCRUBBED GAS

1. Apparatus (see Figure 69)

a. Sampling

(1) Probe - Pyrex® glass probe 7 mm I.D. and of sufficient length for the inlet to be at midstream (centroid) of the stack.

(2) Midget impingers - two.

(3) Filters and casing - millepore. Type AA, 0.8 μ opening with a fiberglass filter for support.

(4) Critical orifice - 26G-3/8 in. needle allowing a flow rate of about 0.3 liter/min.

(5) Vacuum pump - To pull stack gas through the train.

(6) Rotometer - For checking the dry gas flow rate through the sampling train, 0 to 0.5 liter/min.

(7) Septum - Seven millimeters.

(8) Automatic pipette - Delivery capacity 20 ml.

b. Sample Recovery

(1) Glass wash bottles - two.

(2) Sample containers - One ounce French Squares.

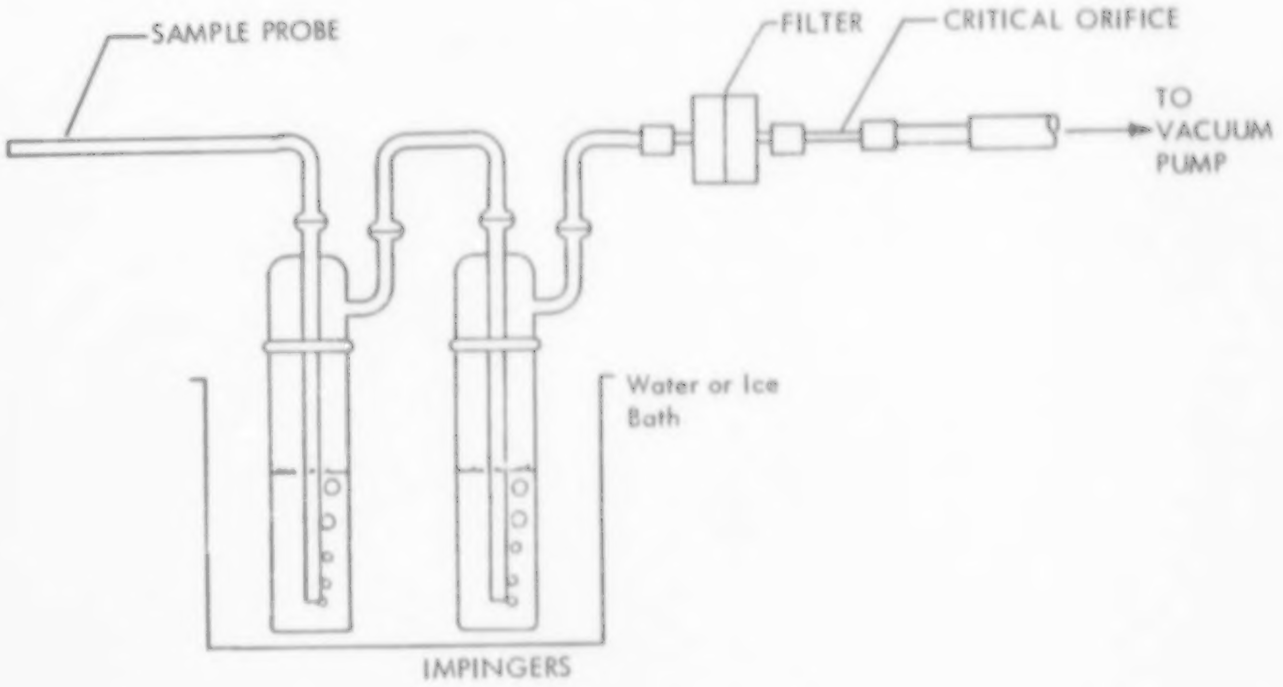


Figure 69. Gas sampling train

2. Reagents

a. Solvent(s) - Pesticide grade as appropriate to the pesticide being tested, see Table 92.

b. Water - Distilled, deionized.

c. Acetone - Reagent grade.

d. Chromic acid - 160 ml concentrated sulfuric acid added to 100 ml saturated potassium dichromate.

3. Procedure

a. Wash Procedure - For sample bottles and caps, probe, impingers, and filters.

(1) Detergent and water.

(2) Rinse twice in tap water.

(3) Chromic acid rinse.

(4) Deionized, distilled water rinse twice.

(5) Acetone rinse - Except filter casings.

(6) Oven dry - 110°C.

b. Train Preparation

(1) Pipette 20 ml of solvent into each of two impingers.

(2) Transfer a fiberglass filter and a Type AA millepore filter to the casing with clean tongs. Assemble the filter casing and tape closed with masking tape.

(3) Assemble the trains as shown in Figure 69.

(4) Tape the probe closed with masking tape to prevent contamination during transport and installation.

c. Sampling

(1) Install the trains at Sampling Points Nos. ⑤, No. ⑦, and No. ⑨, see Figure 5, p. 27.

(2) Check the gas flow rate with a rotometer. The probe should be temporarily disconnected.

(3) Sample the stack gas 30 min.

(4) Again check the gas flow rate, as above, at the end of the experimental test.

d. Sample Recovery

(1) Transfer the contents of the impingers into separate sample bottles.

(2) Tape the filter casing closed for shipment intact.

(3) Send as blanks, samples of solvent, acetone and deionized, distilled water in separate bottles.

(4) Send as a blank an assembled filter and casing properly taped closed.

E. SCRUBBER LIQUIDS

1. Scrubber No. 1 - Hold Tank

a. Initial Sample

(1) Pump to the outside hold tank the water collected during the warm-up phases of the experimental test, leaving approximately 3 in. in the tank.

(2) Rinse twice the weighted sampling bottle with water from the tank.

(3) Collect a sample of Scrubber No. 1 hold tank with the weighted sampling bottle.

(4) Measure the level of water in Scrubber No. 1 hold tank.

B. Final Sample

(1) Rinse the weighted sampling bottle twice with water from Scrubber No. 1 hold tank.

(2) Collect a sample.

(3) Measure the final level of water in the tank.

2. Scrubber No. 2 - Initial and Final Samples

a. Allow the pump to circulate the hexylene glycol in Scrubber No. 2 at least 15 min.

b. Determine the level of Scrubber No. 2 in the sight glass.

c. Purge the sample line and valve by draining and collecting approximately 1 pint of the hexylene glycol.

d. Fill the sample bottle.

3. Scrubber No. 3 - Hold Tank

a. Initial Sample

(1) Pump outside the water collected during the preliminary steps of the test to a level of approximately 1-1/2 in.

(2) Rinse the weighted sampling bottle, reserved for Scrubber No. 3, twice with the water being sampled.

(3) Collect a sample.

(4) Measure the water level of Scrubber No. 3 hold tank.

b. Final Sample

(1) Rinse the weighted sampling bottle twice.

(2) Collect a sample of the Scrubber No. 3 hold tank.

(3) Measure the final water level.

F. SOLID RESIDUES

1. Primary Chamber

a. Remove Thermocouples Nos. 1, 2, and 3

b. Remove the bricks from the underfire air opening.

c. Using a foxtail brush reserved for cleaning out the incinerator, sweep all residue from the front of the chamber to the back of the chamber. Repeat this step as necessary.

d. Remove the residue from the chamber with a vacuum cleaner reserved for cleaning the incinerator only.

e. Transfer the residue from the vacuum cleaner to a tared container(s).

f. Weigh the residue and container(s) and record the weight of the residue.

g. Sample the residue, obtaining representative residue from the top, middle, and bottom portions of the container.

h. Label the container(s) and store.

i. Repeat this procedure after each solid formulation experimental test.

2. Secondary Chamber

a. With compressed air, blow all loose residue from the square stack into the second chamber.

b. Remove the bricks from the door opening in the secondary chamber.

c. Using a foxtail brush reserved for cleaning out the incinerator, sweep all residue from the walls of the chamber to the back of the chamber. Repeat this step as necessary.

d. Remove the residue from the chamber with a vacuum cleaner reserved for cleaning the incinerator only.

e. Transfer the residue from the vacuum cleaner to a tared container.

f. Weigh the residue and container and record the weight of the residue.

g. Sample the residue, obtaining representative residue from the top, middle, and bottom portions of the container.

h. Label the container and store.

i. Repeat this procedure after each solid formulation experimental test.

3. Square Stack

a. With compressed air, blow all loose residue from the bottom of the square stack.

b. Gently tap the outside walls of the square stack with a rubber hammer.

c. With a long brush reserved for cleaning the square stack, pull the residue out into a tared sample container.

d. Weigh the residue, record and label the sample.

e. Repeat this procedure after each solid formulation experimental test.

4. Vertical Stack

a. Clean the primary and secondary chambers and the square stack.

b. Starting at the top of the vertical stack, force a compressed air hose down the stack. Twist the hose back and forth to direct compressed air at the entire circumference of the stack. Repeat this step as necessary.

c. Gently tap the top portion of the vertical stack with a rubber hammer.

d. Blow the residue from the square stack into the secondary chamber.

e. Clean the primary and secondary chambers as previously described.

f. Weigh the residue in a tared container and record.

g. Sample the residue, label and store.

h. Sample the vertical stack only after the concluding pesticide solid formulation experimental test.

5. Horizontal Stack

a. Clean and sample Scrubber No. 1 tank as described below.

b. Take the horizontal stack apart at the seam near the pitot tube.

c. Vacuum in both directions from the seam, using the rigid extentions on the vacuum cleaner.

d. With compressed air, blow any remaining residue from the horizontal stack into either the vertical stack or into Scrubber No. 1 as appropriate.

e. Clean the incinerator and Scrubber No. 1.

f. Weigh the residue, sample, label and store.

g. Sample the horizontal stack after concluding the respective solid formulation tests.

6. Scrubber No. 1

a. Drain Scrubber No. 1.

b. Remove the outlet section containing the demister pad.

c. If there is any residue either in the demister pad or on the walls of the exit section, retain a sample of the residue and label as Exit Scrubber No. 1.

d. Clean Scrubber No. 1 tank with a putty knife.

e. Sample the residue from Scrubber No. 1 tank, label the residue and store.

f. Sample Scrubber No. 1 only after the concluding pesticide solid formulation experimental test.

II. OTHER SAMPLING AND ANALYSIS

A. Sulfur Dioxide

1. Principle

A gas sample is extracted from the sampling point in the stack (Sample Point No. ②) and the acid mist including sulfur trioxide is separated from the sulfur dioxide. The sulfur dioxide fraction is measured by the barium-thorin titration method.

2. Apparatus

a. Sampling (see Figure 70)

(1) Probe - Pyrex® glass, approximately 5 to 6 mm I.D., with a heating system to prevent condensation and a filter to remove particulate matter including sulfuric acid mist.

(2) Midget bubbler - One, with glass wool packed in top to prevent sulfuric acid mist carryover.

(3) Glass wool.

(4) Midge impingers - four.

(5) Silica gel - To dry the sample.

(6) Pump - Leak-free, vacuum type.

(7) Rate meter - Rotometer, or equivalent, to measure a 0 to 10 cubic ft^2/hr flow range.

(8) Dry gas meter - Sufficiently accurate to measure the sample volume within 1%.

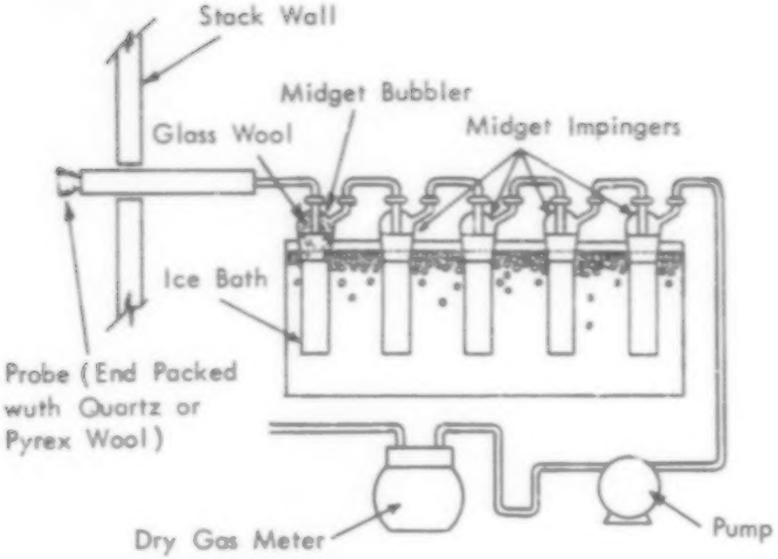


Figure 70. SO_2 sampling train

b. Sample Recovery

(1) Glass wash bottles - Two.

(2) Polyethylene storage bottles - To store impinger samples.

c. Analysis

(1) Pipettes - Transfer type, 5 ml and 10 ml sizes (0.1-ml divisions) and 25-ml size (0.2-ml divisions).

(2) Volumetric flasks - 50 ml, 100 ml and 1,000 ml.

(3) Burettes - 5 ml and 50 ml.

(4) Erlenmeyer flask - 125 ml

3. Reagents

a. Sampling

(1) Water - Deionized, distilled.

(2) Isopropanol, 80% - Mix 80 ml of isopropanol with 20 ml of distilled water.

(3) Hydrogen peroxide, 3% - Dilute 10 ml of 30% hydrogen peroxide with 90 ml of distilled water. Prepare fresh daily.

b. Sample Recovery

(1) Water - Deionized, distilled.

(2) Isopropanol, 80%.

c. Analysis

(1) Water - Deionized, distilled.

(2) Isopropanol.

(3) Thorin indicator - 1-(*o*-Arsonophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt (or equivalent). Dissolve 0.20 g in 100 ml distilled water.

(4) Barium perchlorate (0.01 N) - Dissolve 1.95 g of barium perchlorate [$Ba(ClO_4)_2 3H_2O$] in 200 ml distilled water and dilute to 1 liter with isopropanol. Standarize with sulfuric acid.

(5) Sulfuric acid standard (0.01 N) - Purchase or standardize against a primary standard to ± 0.0002 N.

4. Procedure

a. Sampling

(1) Preparation of collection train - Pour 15 ml of 80% isopropanol into the midget bubbler and 15 ml of 3% hydrogen peroxide to each of the first two midget impingers. Leave the third midget impinger dry. In the final impinger, place approximately 15 ml of silica gel. Assemble the train as shown in Figure 70. Leak check the sampling train at the sampling site by plugging the probe inlet and pulling a 10-in. Hg vacuum. A leakage rate not in excess of 1% of the sampling rate is acceptable. Carefully release the probe inlet plug and turn off the pump. Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 70°F or less.

(2) Sample collection - Adjust the sample flow rate to obtain approximately 1 cu ft in 30 or 60 min as determined by the experimental test. Take readings every 5 min. At the conclusion of each run, turn off the pump and record the final readings. Remove the probe from the stack and disconnect it from the train. Drain the ice bath and purge the remaining part of the train by drawing clean ambient air through the system for 15 min.

b. Sample Recovery - Disconnect the impingers after the purging period. Discard the contents of the midget bubbler. Pour the contents of the midget impingers into a polyethylene shipment bottle. Rinse the three midget impingers and the connecting tubes with distilled water and add these washings to the same storage container.

c. Sample Analysis - Transfer the contents of the storage container to a 50-ml volumetric flask. Dilute to the mark with deionized, distilled water. Pipette a 10 ml aliquot of this solution to a 125-ml Erlenmeyer flask. Add 40 ml of isopropanol and two to four drops of thorin indicator. Titrate to a pink endpoint using 0.01 N barium perchlorate. Run a blank with each series of samples.

5. Calibration

a. Use standard methods and equipment to calibrate the orifice meter, pitot tube, dry gas meter, and probe heater.

b. Standardize the sulfuric acid with potassium acid phthlate as a primary standard. Standardize the barium perchlorate with 25 ml of standard sulfuric acid containing 100 ml of isopropanol.

6. Calculations

a. Dry gas volume - Correct the sample volume measured by the dry gas meter to standard conditions (70°F and 29.92 in. Hg) by using Eq. C-9.

$$V_{m_{std}} = V_m \left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}}{P_{std}}\right) = \left(17.71 \frac{°R}{\text{in. Hg}}\right) \frac{V_m P_{bar}}{T_m} \qquad \text{(C-9)}$$

where $V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cubic feet

V_m = Volume of gas sample through the dry gas meter (meter conditions), cubic feet

T_{std} = Absolute temperature at standard conditions, 530°R

T_m = Average dry gas meter temperature, °R

P_{bar} = Barometric pressure at the orifice meter, in. Hg

P_{std} = Absolute pressure at standard conditions, 29.92 in. Hg

b. Sulfur Dioxide Concentration

$$C_{SO_2} = \left(7.05 \times 10^{-5} \frac{\text{lb-}\ell}{\text{g-ml}}\right) \frac{(V_t - V_{tb})\ (N)\ \left(\frac{V_{soln}}{V_a}\right)}{V_{m_{std}}} \qquad \text{(C-10)}$$

where C_{SO_2} = Concentration of sulfur dioxide at standard conditions, dry basis, lb/ft^3

7.05×10^{-5} = Conversion factor including the number of grams per gram equivalent of sulfur dioxide (32 g/g-eq.), 453.6 g/lb and 1,000 ml/ℓ, lb-ℓ/g-ml

V_t = Volume of barium perchlorate titrant used for the sample, ml

V_{tb} = Volume of barium perchlorate titrant used for the blank, ml

N = Normality of barium perchlorate titrant, g-eq/liter

V_{soln} = Total volume of sample, ml

V_a = Volume of sample aliquot titrated, ml

Adapted from Federal Register, Vol. 36, No. 247, Thursday, 23 December 1971.

B. NITROGEN OXIDES

1. Principle - A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimetrically using the phenoldisulfonic acid (PDS) procedure.

2. Apparatus

a. Sampling (See Figure 71)

(1) Probe - Pyrex® glass, heated, with filter to remove particulate matter. Heating is unnecessary if the probe remains dry during the purging period.

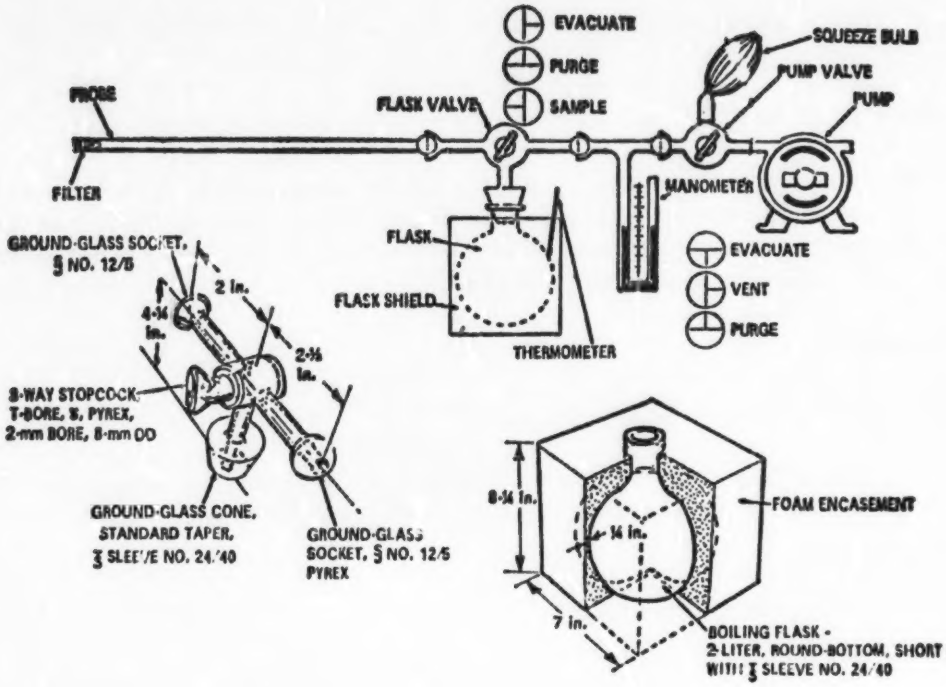

EVACUATE
PURGE
SAMPLE
SQUEEZE BULB
PUMP VALVE
PUMP
PROBE
FLASK VALVE
FILTER
MANOMETER
FLASK
EVACUATE
VENT
PURGE
FLASK SHIELD
THERMOMETER
GROUND-GLASS SOCKET, § NO. 12/5
2 in.
4-¼ in.
2-½ in.
3-WAY STOPCOCK: T-BORE, ꞩ, PYREX, 2-mm BORE, 8-mm OD
GROUND-GLASS CONE, STANDARD TAPER, ꞩ SLEEVE NO. 24/40
GROUND-GLASS SOCKET, § NO. 12/5 PYREX
8-¼ in.
FOAM ENCASEMENT
¼ in.
7 in.
BOILING FLASK - 2-LITER, ROUND-BOTTOM, SHORT NECK, WITH ꞩ SLEEVE NO. 24/40

Figure 71. Sampling train, flask valve, and flask

(2) Collection flask - Two-liter, Pyrex® round bottom with short neck and 24/40 standard taper opening, protected against implosion or breakage.

(3) Flask valve - T-bore stopcock connected to a 24/40 standard taper joint.

(4) Temperature gauge - Dial-type thermometer, or equivalent, capable of measuring 2°F intervals from 25 to 125°F.

(5) Vacuum line - Tubing capable of withstanding a vacuum of 3-in. Hg absolute pressure, with "T" connection and T-bore stopcock, or equivalent.

(6) Pressure gauge - U-tube manometer, 36 in., with 0.1-in. divisions, or equivalent.

(7) Pump - Capable of producing a vacuum of 3-in. Hg absolute pressure.

b. Sample Recovery

(1) Pipette or dropper.

(2) Glass storage containers - Cushioned for shipping.

(3) Glass wash bottle.

c. Analysis

(1) Steam bath.

(2) Beakers or casseroles - 250 ml, one for each sample and standard (blank).

(3) Volumetric pipettes - 1, 2, and 10 ml.

(4) Transfer pipette - 10 ml with 0.1-ml divisions.

(5) Volumetric flask - 100 ml, one for each sample, and 1,000 ml for the standard (blank).

(6) Spectrophotometer - To measure absorbance at 420 mμ.

(7) Graduated cylinder - 100 ml with 1.0-ml divisions.

(8) Analytical balance - To measure to 0.1 mg.

3. Reagents

a. Sampling

(1) Absorbing solution - Add 2.8 ml of concentrated H_2SO_4 to 1 liter of distilled water. Mix well and add 6 ml of 3% hydrogen peroxide. Prepare a fresh solution weekly and do not expose to extreme heat or direct sunlight.

b. Sample Recovery

(1) Sodium hydroxide (1 N) - Dissolve 40 g NaOH in distilled water and dilute to 1 liter.

(2) Red litmus paper.

(3) Water - Deionized, distilled.

c. Analysis

(1) Fuming sulfuric acid - 15 to 18 N by weight free sulfur trioxide.

(2) Phenol - White solid reagent grade.

(3) Sulfuric acid - Concentrated reagent grade.

(4) Standard solution - Dissolve 0.5495 g potassium nitrate (KNO_3) in distilled water and dilute to 1 liter. For the working standard solution, dilute 10 ml of the resulting solution to 100 ml with distilled water. One milliliter of the working standard solution is equivalent to 25 μg nitrogen dioxide.

(5) Water - Deionized, distilled.

(6) Phenoldisulfonic acid solution - Dissolve 25 g of pure white phenol in 150 ml concentrated sulfuric acid on a steam bath. Cool, add 75 ml fuming sulfuric acid, and heat at 100°C for 2 hr. Store in a dark stoppered bottle.

4. Procedure

a. Sampling

(1) Pipette 25 ml of absorbing solution into a sample flask. Insert the flask valve stopper into the flask with the valve in the "purge" position. Assemble the sampling train as shown in Figure 70 and place the probe at the sampling point. Turn the flask valve and the pump valve to their "evacuate" positions. Evacuate the flask to at least 3-in Hg absolute pressure. Turn the pump valve to its "vent" position and turn off the pump. Check the manometer for any fluctuation in the mercury level. If there is a visible change over the span of 1 min, check for leaks. Record the initial volume, temperature, and barometric pressure. Turn the flask valve to its "purge" position, and then do the same with the pump valve. If condensation occurs in the probe and flask valve area, heat the probe and purge until the condensation disappears. Then turn the pump valve to its "vent" position. Turn the flask valve to its "sample" position and allow sample to enter the flask for about 15 sec. After collecting the sample, turn the flask valve to its "purge" position and disconnect the flask from the sampling train. Shake the flask for 5 min.

b. Sample Recovery

(1) Let the flask sit for a minimum of 16 hr and then shake the contents for 2 min. Connect the flask to a mercury-filled U-tube manometer, open the valve from the flask to the manometer, and record the flask pressure and temperature along with the barometric pressure. Transfer the flask contents to a container for shipment or to a 250-ml beaker for analysis. Rinse the flask with two portions of water (approximately 10 ml) and add rinse water to the sample. For a blank use 25 ml of absorbing solution and the same volume of distilled water as used in rinsing the flask. Prior to shipping or analysis, add sodium hydroxide (1 N) dropwise into the sample and the blank until alkaline to litmus paper (about 25 to 35 drops in each).

c. Analysis

(1) If the sample has been shipped in a container, transfer the contents to a 250-ml beaker using a small amount of water. Evaporate the solution to dryness on a steam bath and then cool. Add 2 ml phenoldisulfonic acid solution to the dried residue and triturate thoroughly with a glass rod. Make sure the solution contacts all the residue. Add 1 ml water and 4 drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 min with occasional stirring. Cool, add 20 ml water, mix well by stirring, and add concentrated ammonium hydroxide dropwise

with constant stirring until alkaline to litmus paper. Transfer the solution to a 100-ml volumetric flask and wash the beaker three times with 4- to 5-ml portions of water. Dilute to the mark and mix thoroughly. If the sample contains solids, transfer a portion of the solution to a clean, dry centrifuge tube and centrifuge, or filter a portion of the solution. Measure the absorbance of each sample at 420 mμ using the blank solution as a zero. Dilute the sample and the blank with a suitable amount of distilled water if absorbance falls outside the range of calibration.

5. Calibration

a. Flask Volume - Assemble the flask and flask valve and fill with water to the stopcock. Measure the volume of water to ±10 ml. Number and record the volume on the flask.

b. Spectrophotometer - Add 0.0 to 16.0 ml of standard solution to a series of beakers. To each beaker add 25 ml of absorbing solution and add sodium hydroxide (1 N) dropwise until alkaline to litmus paper (about 25 to 35 drops). Follow the analysis procedure described in (c.) on the previous page to collect enough data to draw a calibration curve of concentration in micrograms, NO_2 per sample versus absorbance.

6. Calculations

a. Sample Volume

$$V_{sc} = \frac{T_{std}(V_t - V_a)}{P_{std}} \left(\frac{P_f}{T_f} - \frac{P_i}{T_i}\right) = \left(17.71 \frac{°R}{\text{in. Hg}}\right)(V_f - 25 \text{ ml}) \left(\frac{P_f}{T_f} - \frac{P_i}{T_i}\right) \quad \text{(C-11)}$$

where V_{sc} = Sample volume at standard conditions (dry basis), ml

T_{std} = Absolute temperature at standard conditions, 530°R

P_{std} = Pressure at standard conditions, 29.92 in. Hg

V_f = Volume of flask and valve, ml

V_a = Volume of absorbing solution, 25 ml

P_f = Final absolute pressure of flask, in. Hg

P_i = Initial absolute pressure of flask, in. Hg

T_f = Final absolute temperature of flask, °R

T_i = Initial absolute temperature of flask, °R

b. Sample Concentration - Read µg NO_2 for each sample from the plot µg NO_2 versus absorbance.

$$c = \left(\frac{m}{V_{sc}}\right)\left(\frac{1\ \text{lb/cu ft}}{1.6 \times 10^4\ \mu\text{g ml}}\right)' = \left(6.2 \times 10^{-5}\ \frac{\text{lb/scf}}{\mu\text{g/ml}}\right)\left(\frac{m}{V_{sc}}\right) \quad \text{(C-12)}$$

where c = Concentration of NO_x as NO_2 (dry basis), lb/scf

m = Mass of NO_2 in gas sample, µg

V_{sc} = Sample volume at standard conditions (dry basis), ml

Adapted from Federal Register, Vol. 36, No. 247, Thursday, 23 December 1971.

C. MOISTURE

1. Principle - Moisture is removed from the gas stream, consensed, and determined gravimetrically.

2. Apparatus (see Figure 72)

a. Probe - Pyrex® glass sufficiently heated to prevent condensation and equipped with a filter to remove particulate matter.

b. Impingers - Three midget impingers, each with 30 ml capacity.

c. Ice Bath Container - To condense moisture in impingers.

d. Rotameter - To measure a flow range from 0 to 1.0 liters/min.

e. Critical Orifice - 22G-1 in. needle allowing a flow of approximately 0.8 liters of dry gas per minute.

f. Pump - Leak-free, diaphragm type, to pull gas through train.

g. Balance - Capable of measuring to the nearest 0.1 g.

h. Barometer - Sufficient to read to within 0.1 in. Hg.

i. Silica gel.

j. Millepore Filter - Type SC, 8.0 μ.

3. Procedure

a. Place about 5 ml distilled water in each of two impingers, and about 15 ml of silica gel in the third impinger.

b. Assemble the train with the water impingers first and second and the silica gel impinger third.

c. Weigh the impingers and contents to the nearest 0.1 g and record.

d. Place the train in the ice bath container.

e. Attach the critical orifice for flow control.

f. Attach the vacuum pump.

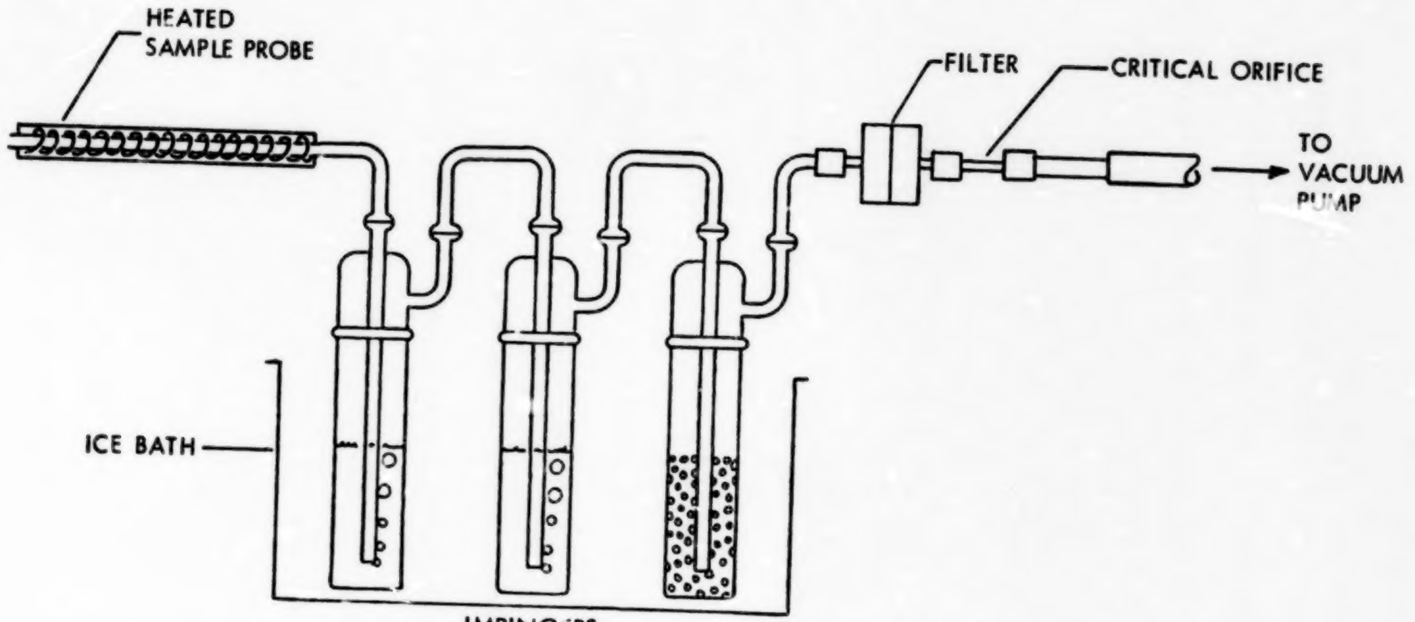


Figure 72. Moisture sampling train

g. Measure the flow with the rotameter and record. Probe should not be in place while checking the flow.

h. Attach the probe and sample the stack 30 or 60 min as appropriate to the experimental test. Record the elapsed time of sampling.

i. After the experimental test, again check the flow as in (g.) above.

j. After collecting the sample, weigh the impingers and their contents again to the nearest 0.1 g.

4. Calculations

a. Volume of Water Collected

$$V_{wc} = \frac{(W_f - W_i)RT_{std}}{P_{std}M_w} = \left(0.0474 \frac{ft^3}{g}\right)(W_f - W_i) \qquad \text{(C-13)}$$

where V_{wc} = Volume of water vapor collected (standard conditions), cu ft

W_f = Final weight of impingers and contents, g

W_i = Initial weight of impingers and contents, g

R = Ideal gas constant, 21.83-in. Hg - cu ft/lb mole-° R

T_{std} = Absolute temperature at standard conditions, 530°R

P_{std} = Pressure at standard conditions, 29.92 in. Hg

M_w = Molecular weight of water, 18 lb/lb-mole

b. Volume of Stack Gas

$$V_m = \frac{F \times M}{28.32 \text{ l/cu ft}} \qquad \text{(C-14)}$$

where V_m = Dry gas volume measured by rotameter, cu ft

F = Average critical orifice flowrate, liters per minute

M = Elapsed time of the test, minutes

c. Gas Volume

$$V_{mc} = V_m \frac{P_m}{P_{std}} \frac{T_{std}}{T_m} = 17.71 \frac{°R}{\text{in. Hg}} \frac{V_m P_m}{T_m} \qquad (C\text{-}15)$$

where V_{mc} = Dry gas volume through train at standard conditions, cu ft

V_m = Dry gas volume measured by rotameter, cu ft

P_m = Barometric pressure, in. Hg

P_{std} = Pressure at standard conditions, 29.92 in. Hg

T_{std} = Absolute temperature at standard conditions, 530°R

T_m = Absolute temperature at critical orifice, 510°R

d. Moisture Content

$$B_{wo} = \frac{V_{wc}}{V_{wc} + V_{mc}} + B_{wm} = \frac{V_{wc}}{V_{wc} + V_{mc}} + (0.025) \qquad (C\text{-}16)$$

where B_{wo} = Proportion by volume of water vapor in the gas stream, dimensionless

V_{wc} = Volume of water vapor collected (standard conditions), cu ft

V_{mc} = Dry gas volume through train (standard conditions), cu ft

B_{wm} = Approximate volumetric proportion of water vapor in the gas stream leaving the impingers, 0.025

e. Percent Moisture

$$\% \text{ Moisture (Volume)} = 100 \times B_{wo} \qquad (C\text{-}17)$$

where % Moisture = Percent of stack gas that is moisture, by volume

Adapted from Federal Register, Vol. 36, No. 247, Thursday, 23 December 1971.

D. EXCESS AIR

1. Principle - A grab gas sample is extracted from a sampling point and analyzed for its components using an Orsat analyzer.

2. Apparatus

a. Grab Sample.

(1) Probe - Stainless steel or Pyrex® glass, equipped with a filter to remove particulate matter.

(2) 500 cc-Tedlar® bags.

(3) Pump - One-way squeeze bulb to transport gas sample to 500-cc Tedlar® bags.

b. Analysis

(1) Orsat analyzer.

3. Procedure

a. Grab Sampling

(1) Place the probe in the stack at the sampling point and purge the sampling line.

(2) Draw sample into the Tedlar® bag.

b. Analysis

(1) Determine the CO_2, O_2, and CO concentrations as soon as possible. Make as many passes as are necessary to give constant readings. If more than 10 passes are necessary, replace the absorbing solution.

4. Calculations

a. Carbon dioxide - Average the three consecutive runs and report result to the nearest 0.1% CO_2.

b. Excess air - Use Eq. C-18 to calculate excess air, and average the runs. Report the result to the nearest 0.1% excess air.

$$\% \text{ EA} = \frac{(\% \; O_2) - 0.5(\% \; CO)}{0.264(\% \; N_2) - (\% \; O_2) + 0.5 \; (\% \; CO)} \times 100 \qquad \text{(C-18)}$$

where

% EA = Percent excess air

% O_2 = Percent oxygen by volume, dry basis

% N_2 = Perc[illegible]rogen by volume, dry basis

% CO = Percent carbon monoxide by volume, dry basis

0.264 = Ratio of oxygen to nitrogen in air by volume

Adapted from Federal Register, Vol. 36, No. 247, Thursday, 23 December 1971.

c. Dry Molecular Weight - Use Eq. C-19 to calculate dry molecular weight and average the runs. Report the result to the nearest 0.1%.

$$M_d = 0.44(\%\ CO_2) + 0.32(\%\ O_2) + 0.28(\%\ N_2 + \%\ CO) \qquad (C\text{-}19)$$

where M_d = Dry molecular weight, pound per pound-mole

$\%\ CO_2$ = Percent carbon dioxide by volume, dry basis

$\%\ O_2$ = Percent oxygen by volume, dry basis

$\%\ N_2$ = Percent nitrogen by volume, dry basis

0.44 = Molecular weight of carbon dioxide divided by 100

0.32 = Molecular weight of oxygen divided by 100

0.28 = Molecular weight of nitrogen divided by 100

Adapted from Federal Register, Vol. 36, No. 247, Thursday, 23 December 1971.

E. TOTAL HYDROCARBONS

1. Equipment

a. 1/4 in. O.D. stainless steel tubing.

b. Midget impinger.

c. Glass wool.

d. Beckman Model 6800 gas analyzer.

e. Leeds and Northrup Model 601 recorder.

f. 1/4 in. O.D. stainless steel probe.

2. Reagents

a. Ultra pure hydrogen.

b. Ultra pure air.

c. Standard gas - 5.44 ppm CH_4
1.04 ppm CO

d. Compressed air - Water pumped.

3. Procedure

a. Place the 1/4 in. O.D. stainless steel probe into midstream (centroid) of the stack at Sample Point No. ② .

b. Connect to the probe one end of the 1/4 in. O.D. stainless steel tubing.

c. Connect the other end of the stainless steel tubing to the midget impinger, filled with glass wool. This midget impinger acts as a particulate trap to protect the gas analyzer.

d. Connect the particulate trap to the sample port of the gas analyzer by means of 1/4 in. OD. stainless steel tubing. The particulate trap should be no more than 3 ft from the gas analyzer.

e. Sample and analyze the stack gas continuously and automatically during the experimental test, using the gas analyzer vacuum pump.

f. Standardize the gas analyzer daily with the standard gas.

g. Record the results of the stack gas and the standard gas by means of the Leeds and Northrup Model 601 recorder.

III. SPECIAL ANALYSIS

Solid and liquid formulations of pesticides containing nitrogen (picloram, atrazine, captan and zineb) were analyzed for cyanide (CN^-) content in the off-gas.

Malathion was the only phosphorus-containing pesticide tested. The off-gas of the malathion solid and liquid formulations were analyzed for total pyrophosphate content.

A. CYANIDE (Calculated as CN^-)

1. Apparatus

a. Sampling

(1) Pipette - 20 ml.

(2) Midget impinger - One.

(3) Filter - Millipore, Type AA 0.8 μ opening with fiberglass filter for support.

(4) Critical orifice - 26G-3/8 in. needle allowing a flow rate of about 0.32 liters/min.

(5) Rotameter - Calibrated to measure a flow rate of 0 to 0.5 liters/min.

(6) Connecting glassware.

(7) Wash bottle.

(8) Sample bottles - Three 30-cc French squares.

b. Analysis

(1) Pipette - 1 ml.

(2) Volumetric flask - 5 ml.

(3) Aminco - Bowman spectrophotofluorometer.

2. Reagents

a. Sampling

(1) Sodium hydroxide - Reagent grade.

(2) Water - Deionized, distilled.

b. Sample Recovery - Deionized, distilled water.

c. Analysis

(1) Palladium chelate - Prepared from 8-hydroxy-5-quinolinesulfonic acid (Fisher Scientific) and palladous chloride (Fisher Scientific) as described in Hanker, Gelberg, and Witten.*

(2) Glycine solution - Prepared by dissolving glycine (reagent grade, Fisher Scientific) and sodium chloride (reagent grade, Fisher Scientific) in deionized distilled water.

(3) Sodium hydroxide solution - 0.5 N

(4) Magnesium chloride hexahydrate solution - 1% W/V in deionized distilled water.

(5) Water - Deionized, distilled

(6) Standards - The solid standard, potassium cyanide (Merck) was used to prepare a stock standard of 1,000 µg/ml cyanide and various amounts were used and treated as the samples (below) to produce a linear curve (linear range used: 0.02 to 1.0 µg/ml).

3. Procedure

a. Preparing the Train (Figure 73)

(1) Pipette 20-cc 0.5 N NaOH, discard.

(2) Pipette 20-cc 0.5 N NaOH into a clean 1-oz French square sample bottle and label as the blank.

(3) Pipette 20-cc 0.5 N NaOH into the midget impinger.

(4) Install the cyanide sampling train at the sampling sight.

---

* Hanker, J. S., A. Gelberg, and B. Witten, Anal. Chem., 30(1):93 (1958).

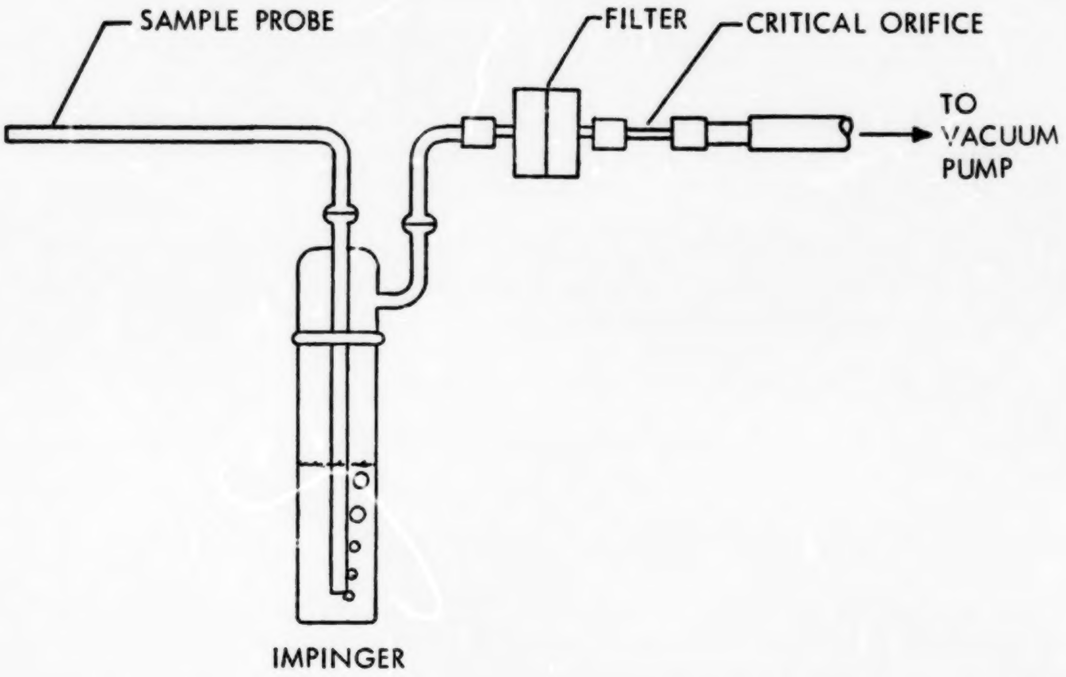


Figure 73. Cyanide sampling train.

(5) Check the needle flow rate by pulling ambient air through a calibrated rotameter, record.

b. Sample the Stack - 30 to 60 min.

c. Sample Recovery

(1) Check the needle flow after the experimental run as in Step (5) above.

(2) Transfer the contents of the impinger into a clean 1-oz French Square sample bottle.

(3) Rinse the impinger with a small volume of distilled water and transfer the rinse to the sample bottle, label.

d. Analysis

(1) Measure total volume of sample.

(2) Pipette into a 5-ml volumetric flask the following: 1 ml of sample; 1 ml of deionized distilled water; 1 ml of glycine-sodium chloride solution; 1 ml of palladium chelate; and 1 ml of magnesium chloride solution.

(3) Shake the volumetric flask vigorously.

(4) After 8 min read a portion on the fluorometer. Excit at 350 nm and measure the fluorescence at 490 nm.

e. Standarization - The standards, which were made up in water contained 1 ml of 0.5 N sodium hydroxide instead of water and were treated identically to the samples.

$$C_{CN} = \frac{Q_{smpl}}{R_c \times T_{smpl}} \times 1 \qquad \text{(C-20)}$$

where C_{CN} = Concentration of cyanide in the stack gas, dry basis, standard conditions, mg/m^3

Q_{smpl} = Amount of cyanide in the sample, μg

R_c = Critical orifice flow rate, dry basis, liters per minute

T_{smpl} = Sampling time, minutes

$$1 = \frac{mg \cdot l}{\mu g \cdot m^3}$$

B. TOTAL PYROPHOSPHATES

1. Apparatus

a. Sampling - Sampling for total pyrophosphates was accomplished as a part of the train sampling for active ingredient and total species in the stack gases.

b. Sample Recovery - Same as for active ingredient and related chemical species.

c. Analysis

(1) Cary 118 ultraviolet - Visible recording spectrophotometer.

(2) Volumetric flasks - Two 25 ml.

(3) Graduated cylinger - 10 ml

2. Reagents

a. Sampling and Sample Recovery

(1) Sulfuric acid - pH 4.

(2) Water - Deionized, distilled.

b. Analysis

(1) Ammonium molybdate - A 5% solution prepared in deionized distilled water.

(2) Ammonium vanadate - 0.25% solution prepared in 2% nitric acid.

(3) Ammonium peroxydisulfate - 7.5% solution prepared in deionized, distilled water.

(4) Standard - 1,000 µg/ml PO_4^{-3} prepared from potassium dihydrogen phosphate in deionized, distilled water.

3. Procedure

a. Sampling and Sample Recovery - Completed during sampling and recovery of the active ingredient and related chemical species train.

b. Analysis - Analysis was performed according to the colorimetric phosphovanadomolybdate procedure first described by Kitson and Mellon.* Two different forms of phosphorus were determined: orthophosphate and total phosphorus (including ortho-, meta-, pyro-, tripoly- and organic phosphates).

(1) Divide the sample into two equal portions, the first for orthophosphate determination and the second for total phosphorus determination.

(2) Transfer the first portion to a 25-ml volumetric flask and add in order: 5 ml of nitric acid (1:2 dilution); 5 ml of ammonium molybdate solution; 5 ml of ammonium vanadate solution; and water to dilute to volume.

(3) Transfer the second portion to a 25-ml volumetric flask and add: 5 ml nitric acid (1:2 dilution) and 5 ml ammonium peroxydisulfate solution. Digest for 10 min on a hot plate. Treat identically to the first portion except exclude the 5 ml addition of nitric acid.

(4) Various amounts of the standard were used to produce a linear curve (linear range used: 0 to 7 μg/ml) when treated with ammonium molybdate and ammonium vanadate.

(5) Scan the samples and standards from 450 nm to 350 nm.

(6) Use water treated with ammonium molybdate and ammonium vanadate as a reference.

---

* Kitson, R. E., and M. G. Mellon, Ind. Eng. Chem. Anal. Ed., **16**:379 (1944).

APPENDIX D

CALCULATIONS

CONTENTS

Page

I. Pesticide and Fuel Oil Rates 390

- Liquid Pesticide Formulations. 390
- Solid Formulations 393

II. Off-Gas Flow Rate. 394

- Stack Gas Velocity 394
- Off-Gas Flow Rate. 394

III. Efficiency of Incineration 395

- Liquid Formulations. 395
- Solid Formulations 396

IV. Retention Time 398

- Primary Chamber. 398
- Secondary Chamber. 399

V. Significant Figures. 399

This appendix contains the important calculations used during the experimental phase of the project and for reduction of the data generated. These calculations are presented using the system of units actually measured, and have not been standardized to the metric system. Calculations pertinent to sampling and analysis have been presented in Appendix C.

Preceding page blank

I. PESTICIDE AND FUEL OIL RATES

A. LIQUID PESTICIDE FORMULATIONS

The liquid pesticide formulations were mixed with fuel oil (or water) to give the approximate primary chamber temperature and active ingredient injection rate desired.

1. Equations for Pesticide Mixing

a. Active ingredient requirement

$$A_o = 1.25\ A_D \qquad \text{(D-1)}$$

where A_o = Amount of contained active ingredient required, pounds

A_D = Predetermined active ingredient injection rate (normally 7.5 or 3.75), pounds per hour

1.25 = Pesticide incineration period, hours

b. Weight of pesticide formulation

$$W_{T_p} = \frac{A_o}{C_o} \times 100 \qquad \text{(D-2)}$$

where W_{T_p} = Weight of pesticide formulation required, pounds

A_o = Amount of weight of active ingredient required, pounds (see (Eq. D-1))

C_o = Active ingredient content of pesticide formulation, percent

c. Volume of pesticide formulation

$$V_p = \frac{W_{T_p}}{(Sp.\ Gr)_p \times 8.34} \qquad \text{(L-3)}$$

where V_p = Volume of pesticide formulation in the mix, gallons

W_{T_p} = Weight of pesticide formulation in the mix, pounds (see (Eq. D-2))

$(Sp.\ Gr)_p$ = Specific gravity of the pesticide formulation

8.34 = Density of water (Sp. Gr = 1.00), pounds per gallon

d. Volume of fuel oil required

$$V_D = 1.25\ R_N - V_p \qquad \text{(D-4)}$$

where V_D = Volume of fuel oil required in the pesticide-fuel oil mixture, gallons

1.25 = Test period, hours

R_N = Burner nozzle flow rate, gallons per hour

V_p = Volume of pesticide formulation in the mix, gallons (see (Eq. D-3))

e. Weight of required fuel oil

$$W_{T_D} = V_D \times (\text{Sp. Gr})_D \times 8.34 \qquad \text{(D-5)}$$

where W_{T_D} = Weight of fuel oil, pounds

V_D = Volume of fuel oil, gallons

$(\text{Sp. Gr})_D$ = Specific gravity of fuel oil

f. Volume fraction of pesticide formulation in total feed

$$B_p = \frac{V_p}{V_p + V_D} \qquad \text{(D-6)}$$

where B_p = Volume fraction of pesticide formulation in the pesticide-fuel oil mixture, gallons per gallon

2. Pesticide and Fuel Oil Injection Rates

a. Total feed rate

$$R_m = \frac{(L_1-L_2) \times 0.2516 \times 60}{(t_2-t_1)} \qquad \text{(D-7)}$$

where R_m = Rate of the pesticide-fuel oil mixture fed to the burner, gallons per hour

L_1 = Initial level of the pesticide formation-fuel oil mixture in the feed drum, centimeters

L_2 = Final level of the pesticide formulation fuel oil mixture in the feed drum, centimeters

0.2516 = Volume per unit height of the feed drum, gallons per centimeter

60 = Minutes per hour

t_1 = Time at L_1 reading, minutes

t_2 = Time at L_2 reading, minutes

b. Pesticide formulation feed rate

$$R_p = B_p \times R_m \qquad \text{(D-8)}$$

where R_p = Pesticide feed rate, gallons per hour

R_m = Total feed rate, gallons per hour (see (Eq. D-6))

B_p = Volume fraction of pesticide formulation (see (Eq. D-6))

c. Fuel oil feed rate

$$R_D = R_m - R_p \qquad \text{(D-9)}$$

where R_D = Fuel oil feed rate, gallons per hour

3. Active Ingredient Injection Rate

$$R_{AI} = C_{AI} \times R_m \times 3{,}785 \qquad \text{(D-10)}$$

where R_{AI} = Pesticide active ingredient feed rate, grams per hour

C_{AI} = Pesticide active ingredient concentration in the pesticide fuel oil mixture, as determined by analysis, grams per milliliter

R_m = Rate of the pesticide-fuel oil mixture fed to the burner, gallons per hour

3,785 = Milliliters per gallon

B. SOLID FORMULATIONS

1. Weight of Solid Pesticide Formulation Burned

$$\text{Net burned} = (G_1 - G_2 - \text{smpl}) \qquad \text{(D-11)}$$

where Net burned = Net weight of the pesticide formulation burned during the experimental test, pounds

G_1 = Gross weight charged into the feeder (including containers), pounds

G_2 = Gross weight remaining in the feeder at the end of the experimental test (including containers), pounds

smpl = Net weight removed from the feeder as samples, pounds

2. Solid Pesticide Feed Rate

$$R_p = \frac{\text{Net burned} \times 60}{(t_2 - t_1)} \qquad \text{(D-12)}$$

where R_p = Rate of solid pesticide fed into the incinerator, pounds per hour

Net burned = Eq. D-10

60 = Minutes per hour

t_2 = Time the feeder was stopped, minutes

t_1 = Time the feeder was started, minutes

3. Active Ingredient Feed Rate

$$R_{AI} = C_{AI} \times R_p \times 4.536 \qquad \text{(D-13)}$$

where R_{AI} = Pesticide active ingredient feed rate, grams per hour

R_p = Rate of solid pesticide formulation feed, pounds per hour

C_{AI} = Pesticide active ingredient concentration in the solid formulation as determined by analysis, percent

$$4.536 = \frac{\text{Grams per pound}}{100}$$

II. OFF-GAS FLOW RATE

A. STACK GAS VELOCITY

$$(V_s)_{avg.} = K_p C_p (\Delta_p)_{avg.} \sqrt{\frac{(T_s)_{avg.}}{P_s M_s}} \times F \qquad \text{(D-14)}$$

where $(V_s)_{avg.}$ = Stack gas velocity, feed per second (fps)

K_p = 85.48 ft/sec (pound per pound mole °R)$^{1/2}$ when these units are used

C_p = Pitot tube coefficient, dimensionless, 0.83

$(T_s)_{avg.}$ = Average absolute stack gas temperature, °R

$(\Delta_p)_{avg.}$ = Average velocity head of stack gas, inches H_2O

P_s = Absolute stack gas pressure, inches Hg

M_s = Molecular weight of stack gas (wet basis), pounds per pound mole

= $M_d(1-B_{wo}) + 18\ B_{wo}$

M_d = Dry molecular weight of stack gas

B_{wo} = Proportion by volume of water vapor in the gas stream

F = Correction factor for the pitot tube in midstream, dimensionless

B. OFF-GAS FLOW RATE

$$Q_s = 3{,}600(1-B_{wo})V_s A \frac{T_{std}}{(T_s)_{avg.}} \frac{P_s}{P_{std}} \qquad \text{(D-15)}$$

where Q_s = Off-gas flow rate, dry basis, standard conditions, cubic feet per hour

A = Cross-sectional area of stack, square feet

T_{std} = Absolute temperature at standard conditions, 530°R

P_{std} = Absolute pressure at standard conditions, 29.92 in. Hg

3,600 = Seconds per hour

III. EFFICIENCY OF INCINERATION
(ACTIVE INGREDIENT AND TOTAL SPECIES BASIS)

A. LIQUID FORMULATIONS

1. Relative Amount of Unburned Pesticide (or Total Species) in Off-Gas

$$\bar{R}_R = \frac{\text{Quantity } \underline{\text{out}}}{\text{Quantity } \underline{\text{in}}} \qquad \text{(D-16)}$$

where $\bar{R}_R$ = Relative amount of unburned pesticide (or total species) in off-gas, grams/hour per gram/hour

a. Quantity out $= \frac{W_{AI}}{R_c \times T_{smpl}} \times Q_s \times 28.32$, grams per hour (D-17)

W_{AI} = Amount of active ingredient (or total species) in the sample by analysis, grams

Q_s = Off-gas flow rate (Eq. D-14), cubic feet per hour

28.32 = Liters per cubic foot

R_c = Critical orifice flow rate, liters per minute

T_{smpl} = Sampling time, minutes

b. Quantity in = R_{AI} (see (Eq. D-10)), grams per hour (D-18)

2. Efficiency

$$\epsilon = [1-\bar{R}_R] \times 100 \qquad \text{(D-19)}$$

where ϵ = Efficiency of incineration (active ingredient or total species basis), percent

$\bar{R}_R$ = Relative amount of unburned pesticide (or total species) in the off gas (Eq. D-16)

3. Concentration of Pesticide (or Total Species) in the Off-Gas

$$C_{off\text{-}gas} = \frac{W_{AI}}{R_c \times T_{smpl}} \times 10^3 \times 10^3 \qquad \text{(D-20)}$$

where $C_{off\text{-}gas}$ = Concentration of active ingredient (or total species) in off gas, milligrams per cubic meter

W_{AI} = Amount of active ingredient (or total species) in the sample by analysis, grams

R_c = Critical orifice flow rate, liters per minute

T_{smpl} = Sampling time, minutes

10^3 = Milligrams per gram

10^3 = Liters per cubic meters

B. SOLID FORMULATIONS

1. Efficiency

$$\epsilon = \left[1 - \frac{\text{quantity } \underline{\text{out}}}{\text{quantity } \underline{\text{in}}}\right] \times 100 \qquad \text{(D-21)}$$

where ϵ = Efficiency of incineration (active ingredient or total species basis), percent

Quantity out = Total quantity of active ingredient (or total species) not burned in the off gas and residue, grams/hour

$$= \frac{\text{Quantity}_{sample} \times Q_s}{V_{m_{std}}} + \text{Quantity}_{residue} \qquad \text{(D-22)}$$

Quantity_{sample} = Total quantity of active ingredient (or total species) in the particulate sampling train, grams

Q_s = Off-gas flow rate (Eq. D-12), cubic feet per hour

$V_{m_{std}}$ = Gas volume sampled, cubic feet

$\text{Quantity}_{residue}$ = Quantity of active ingredient (or total species) in the primary and secondary chamber residues, grams per hour

Quantity $\underline{\text{in}}$ = R_{AI} (see (Eq. D-13)), grams per hour (D-23)

2. Relative Amount of Unburned Pesticide (or Total Species) in the Off-Gas

$$\overline{R}_R = \frac{\text{Quantity}_{\text{off-gas}}}{\text{Quantity } \underline{\text{in}}} \qquad \text{(D-24)}$$

where $\overline{R}_R$ = Relative amount of unburned pesticide (or total species), gram per hour per gram per hour

$$\text{Quantity}_{\text{off-gas}} = \frac{\text{Quantity}_{\text{off-gas}} \times Q_s}{V_{m_{std}}} \qquad \text{(D-25)}$$

$\text{Quantity}_{\text{off-gas}}$ = Total quantity of active ingredient (or total species) in the incinerator effluent sample, grams per hour

Q_s = Off-gas flow rate (Eq. D-12), cubic feet per hour

$V_{m_{std}}$ = Gas volume sampled, cubic feet

$$\text{Quantity } \underline{\text{in}} = R_{AI} \text{ (See (Eq. D-13)} \qquad \text{(D-26)}$$

3. Concentration in Off-Gas

$$C_{\text{off-gas}} = \frac{\text{Quantity}_{\text{sample}} \times 10^3}{V_{m_{std}} \times 0.02832} \qquad \text{(D-27)}$$

where $C_{\text{off-gas}}$ = Concentration of active ingredient (or total species) in the off-gas, milligrams per cubic meter

$\text{Quantity}_{\text{sample}}$ = Total quantity of active ingredient (or total species) in the incinerator effluent sample, grams

10^3 = Milligrams per gram

$V_{m_{std}}$ = Gas volume sampled, standard conditions, cubic feet

0.02832 = Cubic meters per cubic feet

IV. RETENTION TIME

A. PRIMARY CHAMBER

1. Primary Chamber Temperature

$$T_A = \frac{2t_1 + t_2 + 2t_3}{5} + 460 \qquad \text{(D-28)}$$

where T_A = Weighted average temperature of the primary chamber, °R

t_1 = Temperature of Thermocouple No. ⟨1⟩ , °F

t_2 = Temperature of Thermocouple No. ⟨2⟩ , °F

t_3 = Temperature of Thermocouple No. ⟨3⟩ , °F

2. Off-Gas Flow Rate

$$v_A = \frac{(V_s)_{avg.} \times 0.785 \times T_A}{T_7} \qquad \text{(D-29)}$$

where v_A = Off-gas flow rate from the primary chamber at temperature T_A, wet basis, cubic feet per second

T_7 = Temperature of the stack at the pitot tube, °R

(V_s)avg. = Average velocity of the stack gas at T_7 feet per second

0.785 = Cross-sectional area of the stack, square feet

3. Retention Time

$$RT_A = \frac{V_A}{v_A} = \frac{25.6}{v_A} \qquad \text{(D-30)}$$

where RT_A = Retention time of the primary chamber, seconds

V_A = Volume of the primary chamber, cubic feet

v_A = Off-gas flow rate (Eq. D-29), cubic feet per second

B. SECONDARY CHAMBER

1. Secondary Chamber Temperature

$$T_B = \frac{t_4 + t_5}{2} + 460 \qquad \text{(D-31)}$$

where T_B = Average temperature of the secondary chamber, °R

t_4 = Temperature of Thermocouple No. ⟨4⟩, °F

t_5 = Temperature of Thermocouple No. ⟨5⟩, °F

2. Off-Gas Flow Rate

$$v_B = \frac{(V_s)_{avg.} \times 0.785 \times T_B}{T_7} \qquad \text{(D-32)}$$

where v_B = Off-gas flow rate from the secondary chamber at temperature T_B, wet basis, cubic feet per second

3. Retention Time

$$RT_B = \frac{V_B}{v_B} = \frac{20.6}{v_B} \qquad \text{(D-33)}$$

where RT_B = Retention time in the secondary chamber, seconds

V_B = Volume of the secondary chamber, cubic feet

v_B = Off-gas flow rate from the secondary chamber at temperature T_B, wet basis, cubic feet per second (Eq. D-32).

V. SIGNIFICANT FIGURES

Particular attention has been given to the significant figures reported for the relative amounts of unburned pesticides (and total species) and the concentration of pesticides (and total species) in the incinerator off-gas. The calculations used to generate these data for liquid and solid formulations are shown in (Eq. D-16, D-20, D-24, and D-27), respectively. Proper use of significant figures for these results involved a comparison of only the relative uncertainties of the data involved. The rule followed in reporting these values has been that the relative uncertainty of the answer be between 0.2 and 2.0 times the largest relative uncertainty of the data used.

Reference to (Eq. D-16) will show that the calculation of the relative amount of unburned pesticides from liquid formulation tests involves measurements of the amount of pesticide found in the sample train, the sampling rate and time, and the total quantity of incinerator off-gas. In most cases, the greatest relative uncertainty of the measurements involved in this calculation was approximately ± 10%, and was usually associated with the ΔP measurement for total off-gas determination (see (Eq. D-14)). The acceptable relative uncertainty range for reporting the relative rates, therefore, was > 2 to < 20%. The same ranges are applicable to calculations for solid formulation tests. Accordingly, the following significant figures were used.

Value	Percent relative uncertainty
1.0 to 4.9	10 to 2.04
5 to 9	20 to 11.1

For those calculations involving data having a relative uncertainty of > 10%, only one significant figure has been reported.

The calculations for pesticide (and total species) concentration in the effluent gas from liquid and solid pesticide formulation tests are given in (Eqs. D-20 and D-27), respectively. This calculation involves the measurements of amount of pesticide in the sample train, sampling time, and sampling rate (or the volume of gas sampled). The greatest relative uncertainty in these measurements was generally about 5%, and was associated with the volumetric measurements. The acceptable relative uncertainty range for the concentration is between 1 and 10%. These results, therefore, have been reported to two significant figures, i.e., 1.0 to 9.9.